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EQUATIONS FOR THE RAPID MACHINE COMPUTATION OF EQUILIBRIUM COMPOSITION OF AIR AND DERIVATIVES FOR FLOW-FIELD CALCULATIONS

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SUMMARY

Equations are presented for the rapid computation of equilibrium air composition for use in flow-field calculations by electronic computer. The temperature-density domain with temperatures from 1500° K to 15 000° K and densities from 10^2 to 10^{-7} times standard atmospheric density is covered by four equilibrium air models which describe the composition in terms of mole fraction to an accuracy of better than 0.001. Equations are also presented for the computation of partial derivatives of mole fractions with respect to temperature, pressure, and elemental composition.

INTRODUCTION

The rapid computation of the chemical equilibrium composition of air is of great importance in flow-field problems in which a very large number of equilibrium composition calculations must be carried out. The importance of extreme rapidity in this computation is enhanced because, in a Runge-Kutta numerical integration over a single interval, it is necessary to compute the equilibrium composition at each of several steps within the Runge-Kutta procedure. The computation of chemical equilibrium composition may be accomplished by a number of methods. The methods of Brinkley (ref. 1), Huff, Gordon, and Morrell (ref. 2), and White, Johnson, and Dantzig (ref. 3) appear to be the most widely used general methods. A comparative study by Zeleznik and Gordon (ref. 4) showed that none of these methods had any significant computational advantage over the other two. In reference 5, Erickson, Kemper, and Allison show that by reducing the system of equations for a particular chemical system to one equation in one unknown, the unit computational speed may be increased by two orders of magnitude over these three general methods. This gain in computational time is at the expense of tedious algebra in reducing the system to a single equation.

In flow problems with equilibrium chemistry, the partial derivatives of mole (or mass) fractions with respect to pressure and temperature are needed. If diffusion is being considered, so that the elemental composition is variable also, the partial derivatives of mole (or mass) fractions with respect to elemental composition are also needed.

The purpose of this report is to present the application of the method of reference 5 to air over a wide range of temperature and pressure. In this paper, the temperature range from 1500° K to 15 000° K with the density range from 10^2 to 10^{-7} times standard atmospheric density is divided into four regions. Within each region a model of air and the applicable composition equations are set up. Following the method of reference 5, the system of equations for each air model is reduced to one equation in one unknown mole fraction. This equation may be rapidly solved numerically. The remaining concentrations may then be computed from explicit relations. In addition to basic equations for computing composition, this paper also presents these partial derivatives of composition.

SYMBOLS

A	function of x_1 defined by equation (41)
a_m	function of elemental composition defined by equations (31), where subscript m is any integer
B	function of x_1 defined by equation (42)
b_k	ratio of number of species k atoms to number of nitrogen atoms, where subscript k is 2 for oxygen and 3 for argon
D	determinant for equations (37) and (38)
d_n	coefficients in quartic equations, defined by equations (15), (62), and (77) for models A, C, and D, respectively
F_1	function of x_2 defined by equation (A2)
F_8	function of x_7 defined by equation (A22)
F_{11}	function of x_7 defined by equation (A31)

$K_{p,j}$	partial pressure equilibrium constant for reaction j; subscripts for j are given in table II
l	boundary between models
M	mean molecular weight of mixture
M_i	molecular weight of species i
n	integer
p	pressure, atmospheres
R	Universal gas constant
T	temperature, degrees Kelvin
T_2	temperature behind normal shock wave, degrees Kelvin
x_i	mole fraction of species i; subscripts for i are given in table II
α_1,α_2	functions of x_1 defined by equations (33)
β_1,β_2	functions of x_1 defined by equations (35)
γ_m	functions of elemental composition defined by equations (16), where subscript m is any integer
ΔH_j^o	change of enthalpy across reaction j at standard atmospheric pressure
ρ/ρ_o	ratio of density to standard atmospheric density
τ_j	mole fraction equilibrium constant for reaction j; subscripts for j are given in table II

ANALYSIS

The basic approach of dividing the density-temperature domain into four regions, each with its appropriate air model, is first discussed. Next, for each air model, the

equations for equilibrium composition are set up, the method of solution is briefly indicated, and the final equations required for the determination of equilibrium composition are presented. The limitations of each model are then indicated. Finally, the equations for the partial derivatives of composition with respect to pressure, temperature, and composition are presented, with an indication of the method of derivation.

The composition of air is described to a 0.1-percent accuracy with respect to the tables of Hilsenrath and Klein (ref. 6) which were taken as the standard for composition for equilibrium air. The present report does not include gas imperfections, which are considered in reference 6. In figure 1, the air density for which the mole fraction of any given species equals 0.001 is shown as a function of temperature. Thus, for an accuracy of 0.001, a species is present in significant amounts on one side of one of its lines but not on the other side. The symbol for the species appears on the side of the line for which the species is present in amounts greater than a mole fraction of 0.001. After an inspection of figure 1, it was decided to represent the composition of air in different density-temperature regions with four appropriate models as listed in table I. The region of validity of a model is the region within which every species present in a mole fraction of 0.001 or greater is included in the model and is indicated in figure 1 for each of the four models by heavy lines. It is seen that together the four models cover

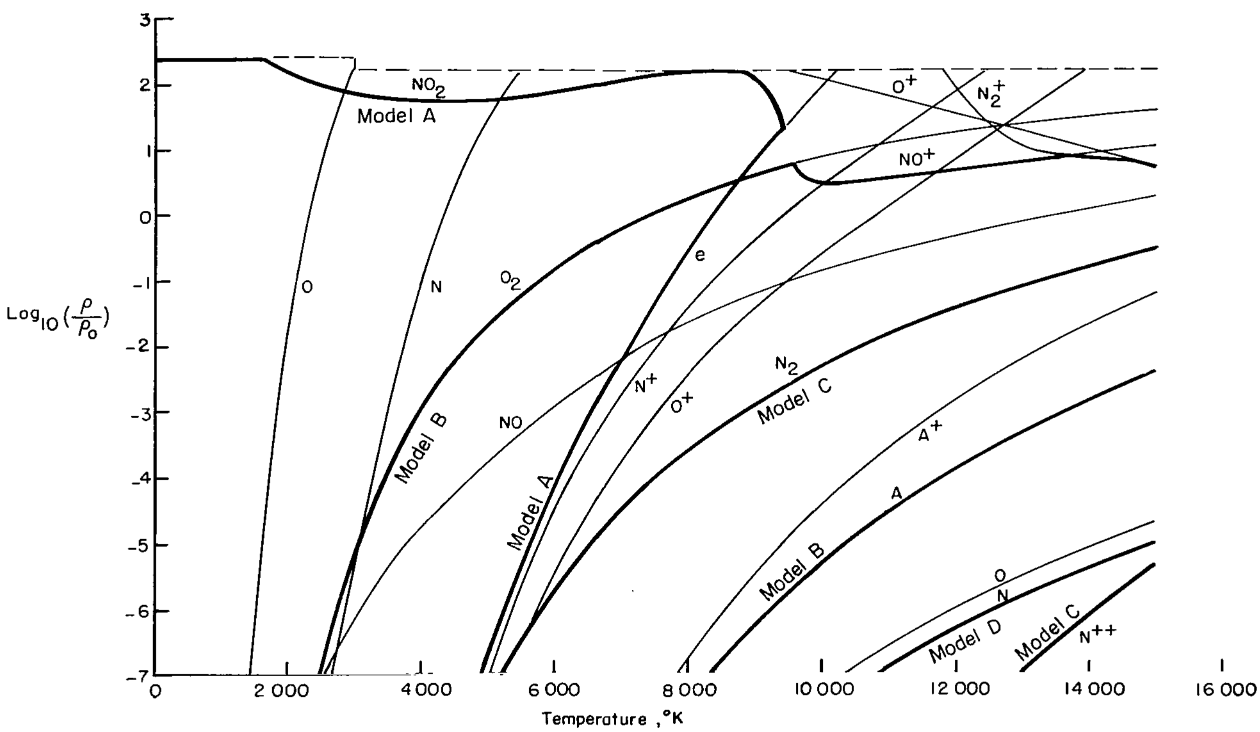

Figure 1.- Lines for mole fraction equal to 0.001 and regions of validity of air models.

the density-temperature domain covered by reference 6 $\left(\text{i.e., } 1500^{\circ}\text{ K} \leqq T \leqq 15\,000^{\circ}\text{ K}; -7 \leqq \log \frac{\rho}{\rho_o} \leqq 2.2 \text{ or } 2.4\right)$ except under conditions of very high density, where species such as NO_2 and N_2^+ become significant. These regions not covered by the four models are not important to the aerodynamicist, inasmuch as they occur only in the stagnation region of a blunt body at velocities exceeding 20 000 ft/sec (6.1 km/sec) at altitudes less than 40 000 ft (12.2 km).

The species are numbered as indicated in table II. Also listed in table II are the nine independent reactions and the corresponding equilibrium constants in terms of mole fractions.

A discussion of the different air models follows.

Model A

Model A is the low temperature model and allows for dissociation and NO formation. The region of validity is limited on the high temperature boundary by the line for electron mole fraction equal to 0.001 and on the high density boundary by the line for NO_2 mole fraction equal to 0.001. In this high density region, gas imperfections are becoming significant, which further limits the accuracy of this model on the high density boundary. Below 1500° K, model A is still valid, but the only significant departure from cold air composition is due to the formation of NO. No computer computations were made for temperatures below 1500° K, but no difficulties are anticipated.

Model A consists of the six species listed in table I: The six equations for model A involving the mole fractions of these species are

$$\tau_1 = x_4 / x_1^2 \tag{1}$$

$$\tau_2 = x_5 / x_2^2 \tag{2}$$

$$\tau_3 = x_6 / x_1 x_2 \tag{3}$$

$$x_3 / (x_1 + 2x_4 + x_6) = b_3 \tag{4}$$

$$(x_2 + 2x_5 + x_6) / (x_1 + 2x_4 + x_6) = b_2 \tag{5}$$

$$x_1 + x_2 + x_3 + x_4 + x_5 + x_6 = 1 \tag{6}$$

Equations (1), (2), and (3) are equilibrium conditions, equations (4) and (5) are mass constraints, and equation (6) follows from definition of mole fraction. Equations (1) to (4) may be used to express x_3, x_4, x_5, and x_6 in terms of x_1 and x_2 as

$$x_4 = \tau_1 x_1^2 \tag{7}$$

$$x_5 = \tau_2 x_2^2 \tag{8}$$

$$x_6 = \tau_3 x_1 x_2 \tag{9}$$

$$x_3 = b_3\left(1 + 2\tau_1 x_1 + \tau_3 x_2\right)x_1 \tag{10}$$

Equations (7) to (10) are used to eliminate x_3 through x_6 in equations (5) and (6). This procedure yields two equations in x_1 and x_2; thus, equations (5) and (6) become, respectively,

$$x_2 + 2\tau_2 x_2^2 + \tau_3 x_1 x_2 = b_2\left(x_1 + 2\tau_1 x_1^2 + \tau_3 x_1 x_2\right) \tag{11}$$

and

$$x_1 + x_2 + b_3\left(x_1 + 2\tau_1 x_1^2 + \tau_3 x_1 x_2\right) + \tau_1 x_1^2 + \tau_2 x_2^2 + \tau_3 x_1 x_2 = 1 \tag{12}$$

Further manipulation yields

$$x_1 = \frac{2b_2 - \gamma_0 x_2 - \gamma_4 x_2^2}{b_2 + \gamma_1 x_2} \tag{13}$$

and, finally,

$$\sum_{n=0}^{4} d_n x_2^n = 0 \tag{14}$$

where

$$\left.\begin{aligned}
d_0 &= b_2^2\left(\frac{1}{\tau_1} + 4\right) \\
d_1 &= -b_2\left(4\gamma_0 + \frac{\gamma_2 - \gamma_1}{\tau_1}\right) \\
d_2 &= \left(\gamma_0^2 - 4b_2\gamma_4\right) - \frac{b_2\gamma_3 + \gamma_1\gamma_2}{\tau_1} \\
d_3 &= 2\gamma_4\gamma_0 - b_2\frac{\tau_2}{\tau_1}\gamma_1 - \frac{\gamma_1\gamma_3}{\tau_1} \\
d_4 &= \gamma_4^2 - \gamma_1^2\frac{\tau_2}{\tau_1}
\end{aligned}\right\} \tag{15}$$

$$\left.\begin{aligned}
\gamma_0 &= 1 + 2(b_2 + b_3) \\
\gamma_1 &= \tau_3(\gamma_0 - b_2) \\
\gamma_2 &= 1 + b_2 + b_3 + \tau_3(1 - b_2) \\
\gamma_3 &= \tau_2(2 + b_2 + 2b_3) + \tau_3(b_2 + b_3) \\
\gamma_4 &= 2\tau_2(\gamma_0 - b_2)
\end{aligned}\right\} \tag{16}$$

Equation (14) is in the form suggested by reference 5 and can be solved quite rapidly by using Newton's iteration scheme. Once x_2 is found, x_1 can be calculated from equation (13), and the remaining species are computed by equations (7) to (10).

Equation (14) has four roots. Only real roots lying between 0 and 1 need be considered. As pointed out in reference 5, for only one of these values of x_2 will the mole fractions of the remaining five species lie between 0 and 1.

Model B

Model B is the most complex of the air models. Covering a wide range of temperatures, model B allows for dissociation, ionization, and formation of NO. The anticipated region of validity of this model was limited by the line for O_2 mole fraction equal to 0.001 on the low temperature boundary, by the line for A^+ mole fraction equal to 0.001 on the high temperature boundary, and by the NO^+ and N_2^+ mole fractions equal to 0.001 on the high density boundary. Unfortunately the full extent of the anticipated region of validity was not realized due to numerical difficulties, which are subsequently discussed. As a consequence, the practical region of validity as limited by these numerical difficulties was found by trial and error to be bounded by the line for electron mole fraction equal to 0.001 on the low temperature boundary. This limitation creates no problem in practice, inasmuch as model A can be used up to this line.

Model B consists of the eight species listed in table I. The eight starting equations for this model are

$$x_4/x_1^2 = \tau_1 \tag{17}$$

$$x_6/x_1x_2 = \tau_3 \tag{18}$$

$$x_1/x_7x_8 = \tau_4 \tag{19}$$

$$x_2/x_7x_9 = \tau_5 \tag{20}$$

$$x_3/(x_1 + x_8 + 2x_4 + x_6) = b_3 \tag{21}$$

$$(x_2 + x_9 + x_6)/(x_1 + x_8 + 2x_4 + x_6) = b_2 \tag{22}$$

$$x_7 = x_8 + x_9 \tag{23}$$

$$x_1 + x_2 + x_3 + x_4 + x_6 + x_7 + x_8 + x_9 = 1 \tag{24}$$

Equations (17) to (20) are equilibrium conditions, equations (21) and (22) are mass constraints, and equation (23) expresses charge neutrality. Equations (17), (18), and (21) may be solved for x_4, x_6, and x_3, respectively, and these unknowns are eliminated from the system of equations by the following substitutions:

$$x_4 = \tau_1 x_1^2 \tag{25}$$

$$x_6 = \tau_3 x_1 x_2 \tag{26}$$

$$x_3 = b_3\left(x_1 + x_8 + 2x_4 + x_6\right) \tag{27}$$

Equation (22) is used to eliminate x_9; thus,

$$x_9 = b_2\left(x_1 + x_8 + 2\tau_1 x_1^2 + \tau_3 x_1 x_2\right) - x_2 - \tau_3 x_1 x_2 \tag{28}$$

Equation (23) is now combined with equation (28) to give the following expression for x_8:

$$x_8 = \left(1 + b_2\right)^{-1}\left[x_7 + x_2 + \tau_3 x_1 x_2 - b_2\left(x_1 + 2\tau_1 x_1^2 + \tau_3 x_1 x_2\right)\right] \tag{29}$$

Next x_7 is solved for from equation (24) with equations (25) to (29) used to eliminate x_3, x_4, x_6, x_8, and x_9. After some manipulation the result is obtained that

$$x_7 = a_0 - a_1 x_1 - a_1 x_2 - a_2 \tau_3 x_1 x_2 - a_2 \tau_1 x_1^2 \tag{30}$$

where

$$\left.\begin{aligned} a_0 &= \left(2 + \frac{b_3}{1 + b_2}\right)^{-1} \\ a_1 &= a_0\left(1 + \frac{b_3}{1 + b_2}\right) \\ a_2 &= a_0\left(1 + \frac{2b_3}{1 + b_2}\right) \end{aligned}\right\} \tag{31}$$

For convenience equation (30) is written as

$$x_7 = \alpha_1 - \alpha_2 x_2 \tag{32}$$

where

$$\left.\begin{aligned} \alpha_1 &= a_0 - a_1 x_1 - a_2 \tau_1 x_1^2 \\ \alpha_2 &= a_1 + a_2 \tau_3 x_1 \end{aligned}\right\} \tag{33}$$

Equation (32) is used in equation (29), whence x_8 may be written as

$$x_8 = \beta_1 + \beta_2 x_2 \tag{34}$$

where

$$\left.\begin{aligned} \beta_1 &= \left(1 + b_2\right)^{-1}\left[a_0 - \left(a_1 + b_2\right)x_1 - \left(a_2 + 2b_2\right)\tau_1 x_1^2\right] \\ \beta_2 &= \left(1 + b_2\right)^{-1}\left[\left(1 - a_1\right) + \left(1 - a_2 - b_2\right)\tau_3 x_1\right] \end{aligned}\right\} \tag{35}$$

Equation (23) gives, by using equations (32) and (34),

$$x_9 = \left(\alpha_1 - \beta_1\right) - \left(\alpha_2 + \beta_2\right)x_2 \tag{36}$$

Thus far, all the species, in particular x_7, x_8, and x_9, can be expressed as very simple functions of x_1 and x_2, which remain undetermined, and equations (19) and (20) have yet to be used. Equations (32), (34), and (36) are used in equations (20) and (21). After some manipulation equations (20) and (21) become

$$-\left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)x_2 + \alpha_2^2 x_2^2 = \frac{1}{\tau_4}x_1 - \alpha_1^2 \tag{37}$$

$$\left(\alpha_1\beta_2 - \alpha_2\beta_1\right)x_2 - \alpha_2\beta_2 x_2^2 = \frac{1}{\tau_4}x_1 - \alpha_1\beta_1 \tag{38}$$

Equations (37) and (38) may be considered to be two equations in two unknowns x_2 and x_2^2; therefore, solving by Kramer's rule gives

$$x_2 = \frac{A}{D/\alpha_2} \tag{39}$$

$$x_2^2 = \frac{B}{D} \tag{40}$$

where

$$A = \alpha_1\alpha_2\beta_1 + \alpha_1^2\beta_2 - \frac{1}{\tau_4}x_1\left(\alpha_2 + \beta_2\right) \tag{41}$$

$$B = \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\left(\alpha_1\beta_1 - \frac{1}{\tau_4}x_1\right) + \left(\alpha_1\beta_2 - \alpha_2\beta_1\right)\left(\alpha_1^2 - \frac{1}{\tau_4}x_1\right) \tag{42}$$

$$\frac{D}{\alpha_2} = \left(\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\beta_2 + \alpha_2^2\beta_1 \tag{43}$$

Equations (39) and (40) give x_2 and x_2^2 as functions of x_1, which is as yet undetermined. The equation for x_1 is obtained by squaring the right-hand side of equation (39)

and setting it equal to the right-hand side of equation (40), whence, after simplification,

$$\left(\frac{D}{\alpha_2}\right)B - \alpha_2 A^2 = 0 \tag{44}$$

Equation (44) has the form $F(x_1) = 0$ and may be solved numerically for x_1, after which the remaining x_i may be computed. In principle, equation (44) may be expanded to give an eleventh-order polynomial; however, in practice, the tedious labor required to carry out this expansion makes it prohibitive to do so, so that equation (44) is used directly.

It was found that for low temperatures where electron concentrations are small, equation (30) is unsuitable for computing x_7 after x_1 has been determined, inasmuch as a small number is obtained by subtracting large numbers with a resulting loss of accuracy. The same problem appears in equations (34) and (36). This problem is circumvented by rewriting equations (19) and (20) as

$$x_7 x_8 = \frac{1}{\tau_4} x_1$$

$$x_7 x_9 = \frac{1}{\tau_5} x_2$$

Adding these two equations and using equation (23) gives

$$x_7 = \sqrt{\frac{1}{\tau_4} x_1 + \frac{1}{\tau_5} x_2} \tag{45}$$

Now x_8 and x_9 can be computed from

$$x_8 = \frac{1}{\tau_4} \frac{x_1}{x_7} \tag{46}$$

$$x_9 = \frac{1}{\tau_5} \frac{x_2}{x_7} \tag{47}$$

Once equation (44) has been solved for x_1, x_2 follows immediately from equation (39). Next x_4, x_6, x_7, x_8, and x_9 are found from equations (25), (26), (45), (46), and (47), and finally x_3 is found from equation (27).

Model C

Model C applies at high temperatures and consists of atoms, ions, and electrons. It is limited on one boundary by the presence of N_2 and on the other boundary by the presence of N^{++}.

Model C contains the seven species listed in table I. The equations used for this model are

$$x_1/x_7x_8 = \tau_4 \tag{48}$$

$$x_2/x_7x_9 = \tau_5 \tag{49}$$

$$x_3/x_7x_{10} = \tau_6 \tag{50}$$

$$(x_2 + x_9)/(x_1 + x_8) = b_2 \tag{51}$$

$$(x_3 + x_{10})/(x_1 + x_8) = b_3 \tag{52}$$

$$x_7 = x_8 + x_9 + x_{10} \tag{53}$$

$$x_1 + x_2 + x_3 + x_7 + x_8 + x_9 + x_{10} = 1 \tag{54}$$

Equations (48), (49), and (50) are equilibrium conditions, equations (51) and (52) are mass constraints, and equation (53) expresses charge neutrality. Equations (48), (49), and (50) may be solved for x_1, x_2, and x_3 to give

$$x_1 = \tau_4 x_7 x_8 \tag{55}$$

$$x_2 = \tau_5 x_7 x_9 \tag{56}$$

$$x_3 = \tau_6 x_7 x_{10} \tag{57}$$

By using equations (55), (56), and (57), equations (51) and (52), respectively, give

$$x_9 = b_2 \frac{1 + \tau_4 x_7}{1 + \tau_5 x_7} x_8 \tag{58}$$

$$x_{10} = b_3 \frac{1 + \tau_4 x_7}{1 + \tau_6 x_7} x_8 \tag{59}$$

Equations (58) and (59) are used in equation (53), whence

$$x_8 = \frac{x_7}{1 + b_2 \dfrac{1 + \tau_4 x_7}{1 + \tau_5 x_7} + b_3 \dfrac{1 + \tau_4 x_7}{1 + \tau_6 x_7}} \tag{60}$$

Thus, only x_7 remains to be determined; equation (54) is the only equation left unused. Equations (55) to (60) are used to express all x_i in equation (54) in terms of x_7. The result, after simplification, is

$$\sum_{n=0}^{4} d_n x_7^n = 0 \tag{61}$$

where

$$\left.\begin{aligned}
d_0 &= -(1 + b_2 + b_3) \\
d_1 &= 2(1 + b_2 + b_3) - (b_2 + b_3)\tau_4 - (b_3 + 1)\tau_5 - (1 + b_2)\tau_6 \\
d_2 &= (1 + 2b_2 + 2b_3)\tau_4 + (2 + b_2 + 2b_3)\tau_5 + (2 + 2b_2 + b_3)\tau_6 \\
&\quad - (\tau_5\tau_6 + b_2\tau_6\tau_4 + b_3\tau_4\tau_5) \\
d_3 &= (1 + b_2 + 2b_3)\tau_4\tau_5 + (2 + b_2 + b_3)\tau_5\tau_6 + (1 + 2b_2 + b_3)\tau_6\tau_4 \\
d_4 &= (1 + b_2 + b_3)\tau_4\tau_5\tau_6
\end{aligned}\right\} \tag{62}$$

Equation (61) can be solved by Newtonian iteration to give x_7. Then, x_8 is computed from equation (60), x_9 and x_{10} from equations (58) and (59), and x_1, x_2, and x_3 from equations (55), (56), and (57).

Model D

Model D applies at extremely high temperature where the air consists of singly and doubly ionized atoms and electrons. It is limited on one boundary by the presence of N; the other boundaries were not considered.

Model D and its equations are analogous to model C and its equations. The atoms and singly ionized atoms of model C correspond directly to the singly and doubly ionized atoms of model D. The equations of model D are

$$x_8/x_7x_{11} = \tau_7 \tag{63}$$

$$x_9/x_7x_{12} = \tau_8 \tag{64}$$

$$x_{10}/x_7x_{13} = \tau_9 \tag{65}$$

$$\left(x_9 + x_{12}\right)/\left(x_8 + x_{11}\right) = b_2 \tag{66}$$

$$\left(x_{10} + x_{13}\right)/\left(x_8 + x_{11}\right) = b_3 \tag{67}$$

$$x_7 = x_8 + x_9 + x_{10} + 2\left(x_{11} + x_{12} + x_{13}\right) \tag{68}$$

$$x_7 + x_8 + x_9 + x_{10} + x_{11} + x_{12} + x_{13} = 1 \tag{69}$$

These equations are required by equilibrium conditions, mass constraints, and charge neutrality.

Solving equations (63), (64), and (65) for x_8, x_9, and x_{10} results in

$$x_8 = \tau_7 x_7 x_{11} \tag{70}$$

$$x_9 = \tau_8 x_7 x_{12} \tag{71}$$

$$x_{10} = \tau_9 x_7 x_{13} \tag{72}$$

Equations (70) to (72) are used in equations (66) and (67) to give

$$x_{12} = b_2 \frac{1 + \tau_7 x_7}{1 + \tau_8 x_7} x_{11} \tag{73}$$

$$x_{13} = b_3 \frac{1 + \tau_7 x_7}{1 + \tau_9 x_7} x_{11} \tag{74}$$

Equations (70) to (74) are used in equation (68) to give the following relation between x_7 and x_{11}:

$$x_{11} = \frac{x_7}{2 + \tau_7 x_7 + b_2\left(\frac{1 + \tau_7 x_7}{1 + \tau_8 x_7}\right)\left(2 + \tau_8 x_7\right) + b_3\left(\frac{1 + \tau_7 x_7}{1 + \tau_9 x_7}\right)\left(2 + \tau_9 x_7\right)} \tag{75}$$

Equations (70) to (75) are used to express all x_i in equation (69) in terms of x_7. The result simplifies to

$$\sum_{n=0}^{4} d_n x_7^n = 0 \tag{76}$$

where

$$\left.\begin{aligned}
d_0 &= -2(1 + b_2 + b_3) \\
d_1 &= 3(1 + b_2 + b_3) - \tau_7(1 + 2b_2 + 2b_3) - \tau_8(2 + b_2 + 2b_3) - \tau_9(2 + 2b_2 + b_3) \\
d_2 &= \tau_7(2 + 3b_2 + 3b_3) + \tau_8(3 + 2b_2 + 3b_3) + \tau_9(3 + 3b_2 + 2b_3) \\
&\quad - \tau_7\tau_8(1 + b_2 + 2b_3) - \tau_8\tau_9(2 + b_2 + b_3) - \tau_9\tau_7(1 + 2b_2 + b_3) \\
d_3 &= \tau_7\tau_8(2 + 2b_2 + 3b_3) + \tau_8\tau_9(3 + 2b_2 + 2b_3) + \tau_9\tau_7(2 + 3b_2 + 2b_3) \\
&\quad - \tau_7\tau_8\tau_9(1 + b_2 + b_3) \\
d_4 &= 2\tau_7\tau_8\tau_9(1 + b_2 + b_3)
\end{aligned}\right\} \tag{77}$$

Equation (76) is solved for x_7 by Newtonian iteration, after which x_{11} is computed from equation (75), x_{12} and x_{13} from equations (73) and (74), and x_8, x_9, and x_{10} from equations (70), (71), and (72).

Partial Derivatives

The partial derivatives of composition with respect to pressure and temperature are now considered. These derivatives enter into a flow problem through the equation of state

$$p = \frac{\rho RT}{M}$$

which is expressed in derivative form as

$$\frac{1}{p}\nabla p = \frac{1}{\rho}\nabla\rho + \frac{1}{T}\nabla T + M\nabla\left(\frac{1}{M}\right)$$

The term $\nabla\left(\frac{1}{M}\right)$ is given by

$$\nabla\left(\frac{1}{M}\right) = -\frac{1}{M^2}\sum_i M_i \nabla x_i$$

For an equilibrium gas

$$\nabla x_i = \left(\frac{\partial x_i}{\partial p}\right)_T \nabla p + \left(\frac{\partial x_i}{\partial T}\right)_p \nabla T$$

In computing $\left(\frac{\partial x_i}{\partial p}\right)_T$ and $\left(\frac{\partial x_i}{\partial T}\right)_p$, the pressure and temperature dependencies are implicit in τ_j. The approach taken in this analysis is to compute the values of $\partial x_i/\partial \tau_j$, after which the desired partial derivatives are given by

$$\left(\frac{\partial x_i}{\partial p}\right)_T = \sum_j \frac{\partial x_i}{\partial \tau_j}\left(\frac{\partial \tau_j}{\partial p}\right)_T$$

$$\left(\frac{\partial x_i}{\partial T}\right)_p = \sum_j \frac{\partial x_i}{\partial \tau_j}\left(\frac{\partial \tau_j}{\partial T}\right)_p$$

where the summations are carried out over only those j values for which τ_j appears in the gas model. All τ_j are defined so that

$$\tau_j = pK_{p,j}$$

Thus,

$$\left(\frac{\partial \tau_j}{\partial p}\right)_T = K_{p,j}$$

$$\left(\frac{\partial \tau_j}{\partial T}\right)_p = p\left(\frac{\partial K_{p,j}}{\partial T}\right)_p = \frac{\Delta H_j^o}{RT^2}\tau_j$$

The equation in one unknown x_I of the form

$$F\left(x_I, \tau_j\right) = 0$$

is differentiated implicitly to give

$$\frac{\partial x_I}{\partial \tau_j} = -\frac{\partial F/\partial \tau_j}{\partial F/\partial x_I}$$

The remaining $\partial x_i/\partial \tau_j$ are derived by differentiating the explicit expressions for each x_i. The derivations are straightforward, and the resulting expressions are listed in appendix A in the order required for computation.

The partial derivatives of mole fractions with respect to elemental composition $\partial x_i/\partial b_k$ are needed for the solution of problems involving diffusion, for example, in boundary layers. Again, the derivations are straightforward, and the resulting expressions are listed in appendix B in the order required for computation.

Minor Species

A simple computation of the concentration of a minor species can be made in which the major species are known from the solution of one of the air models. The method is demonstrated by considering the following example.

Assume that the electron concentration in the region of model A is desired. Electrons are contributed primarily by NO but are also contributed by N and O. The

equations applicable to the problem for the indicated chemical reactions are as follows:

$$N^+ + e = N \qquad x_1/x_7x_8 = \tau_4 \tag{78}$$

$$O^+ + e = O \qquad x_2/x_7x_9 = \tau_5 \tag{79}$$

$$NO^+ + e = NO \qquad x_6/x_7x_{14} = \tau_{10} \tag{80}$$

$$x_7 = x_8 + x_9 + x_{14} \tag{81}$$

In equations (78) to (80), x_1, x_2, and x_6 are known from the major species computation and x_7, x_8, x_9, and x_{14} are unknown minor species. Solving equations (78), (79), and (80) for x_8, x_9, and x_{14} results in:

$$\left.\begin{aligned} x_8 &= \frac{x_1}{\tau_4 x_7} \\ x_9 &= \frac{x_2}{\tau_5 x_7} \\ x_{14} &= \frac{x_6}{\tau_{10} x_7} \end{aligned}\right\} \tag{82}$$

These expressions are substituted in equation (81) to give the following equation for x_7:

$$x_7 = \sqrt{\frac{x_1}{\tau_4} + \frac{x_2}{\tau_5} + \frac{x_6}{\tau_{10}}} \tag{83}$$

The electron concentration is thus quickly computed from equation (83). If desired, the mole fractions of the minor species NO^+, N^+, and O^+ can then be computed from equations (82).

RESULTS AND DISCUSSION

The equations for the four gas models were programed for machine computation, and a number of computations were made to test the accuracy of the gas models in computing composition. No numerical difficulties were encountered with models A, C, or D, but problems were encountered with model B at low temperatures, which effectively limit its region of validity. At very low temperature, x_1 becomes quite small as τ_1, τ_4, and τ_5 become quite large compared with unity, and in equation (44) the terms $\frac{D}{\alpha_2}B$ and $\alpha_2 A^2$ are insensitive to x_1 and are equal to each other to several decimal

places. Practically, equation (44) reduces to an identity and is satisfied quite accurately by a fairly wide range of x_i; this creates a computational problem. Another problem encountered in using model B at low temperatures is that an extraneous root of equation (44) is obtained; however, x_2 computed from this value for x_1 exceeds the bound imposed by the mass balance of the problem so that x_2 can be tested, this root of x_1 rejected, and the search for a satisfactory root continued. None of these problems arise with model B on the high temperature side of the line for electron mole fraction equal to 0.001. (See fig. 1.) Inasmuch as model A is applicable out to this line, all the numerical difficulties associated with model B at low temperatures can be avoided by using model A up to the line for electron mole fraction equal to 0.001. The results of a series of test computations for air composition are listed in table III; also given for comparison are the compositions from reference 6. This comparison indicates that the accuracy of the composition of air as computed from the equations in the present report should be adequate for most purposes.

The boundaries of the gas models, shown in figure 1 as a density-temperature plot, were mapped onto a velocity-altitude plot (fig. 2) by using figure 6 of reference 7. Thus, the temperature and density data in figure 2 correspond to equilibrium conditions immediately behind a normal shock wave. Compositions are listed in reference 6 for temperatures up to 15 000° K. The boundaries below the 15 000° K isotherm were extended out to 50 000 ft/sec (15 km/sec) by using the compositions listed in reference 8. The low density boundary $\left(\log_{10} \frac{\rho}{\rho_0} = -7\right)$ is above an altitude of 400 000 ft (122 km). It is not

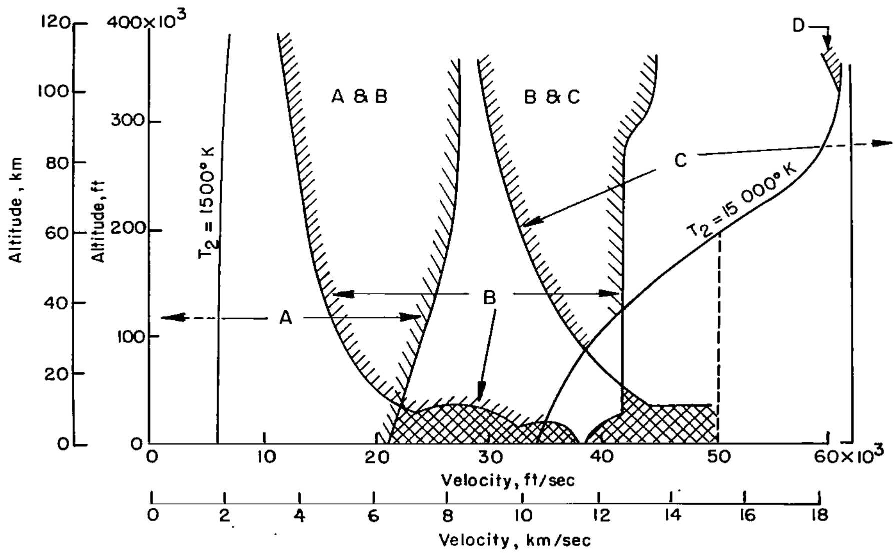

Figure 2.- Velocity-altitude plot of regions of validity of air models. (Data based on conditions immediately behind normal shock.)

likely that equilibrium flow conditions will be of concern above this altitude. The high density region where NO^+ and $N_2{}^+$ are significant maps onto a velocity-altitude region corresponding to orbital velocities below a 40 000-ft (12 km) altitude. These flight conditions are not currently important to the aerodynamicist.

The pressure-temperature boundaries of the four models are shown in figure 3. For purposes of machine computation, quadratic expressions were fitted to the boundaries. The boundaries established by these expressions and indicated in figure 3 by bold lines are:

I: $T \geqq 1500^\circ$ K

II: $T \leqq 15\,000^\circ$ K

III: $\log_{10} p \geqq -4.6 - 0.035\left(15 - \frac{T}{1000}\right) - 0.00556\left(15 - \frac{T}{1000}\right)^2$

IV: $\log_{10} p \leqq 3$

V: $l = 1 + 1.5\left(\frac{T}{1000} - 8\right) - 0.16\left(\frac{T}{1000} - 8\right)^2$

for $\log_{10} p \geqq l$, use model A

for $\log_{10} p < l$, use model B, C, or D

VI: $l = 0.5 + 0.446\left(\frac{T}{1000} - 12\right) - 0.0541\left(\frac{T}{1000} - 12\right)^2$

for $\log_{10} p > l$, use model B

for $\log_{10} p \leqq l$, use model C or D

VII: $l = -2.65 + 0.51\left(\frac{T}{1000} - 15\right)$

for $\log_{10} p \geqq l$, use model C

for $\log_{10} p < l$, use model D

The species listed for model A are adequate for $T < 1500^\circ$ K, but the equations have not been applied in this region to check for numerical difficulties which may arise. Similarly, no check has been made of the models at temperatures above 15 000° K or at pressures below boundary III. Thus, boundaries I, II, and III are included to avoid using the models in untested regions and are not tested bounds on the validity of the models. However, boundary III corresponds to altitudes in excess of 400 000 ft (122 km), and for temperatures below 1500° K the composition of air is essentially that of cold air. Boundary V was placed so as to avoid computational problems with model B by using model A as much as possible, and boundary VI was placed so as to use model C as much as possible, because model C is considerably simpler than model B.

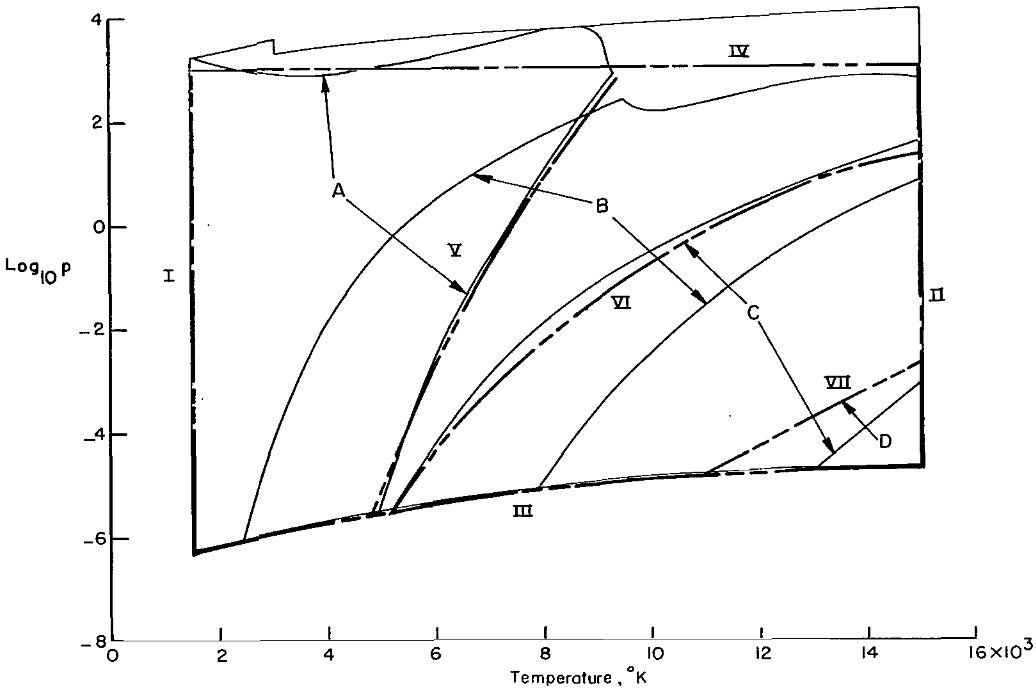

Figure 3.- Pressure-temperature boundaries of air models.

RÉSUMÉ

The computation of air composition has been dealt with by dividing the temperature range between 1500° K and 15 000° K and the density range between 10^2 and 10^{-7} times standard atmospheric density into four regions, within each of which a relatively simple air model may be used for the equilibrium chemical composition. In each air model, the mass constraints and equilibrium conditions, stated as a function of temperature and pressure, are reduced to a single equation in one unknown mole fraction. This equation can be solved numerically, after which the composition of the gas can be rapidly computed from closed-form expressions. The accuracy of the compositions computed by the present method was better than 0.001 in terms of mole fraction.

Equations are also given for partial derivatives of mole fraction with respect to temperature, pressure, and elemental composition.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., April 27, 1967,
124-07-01-29-23.

APPENDIX A

EQUATIONS FOR COMPUTING $\frac{\partial x_i}{\partial \tau_j}$

The equations are presented in the order required for computation for each model. For model A,

$$\frac{\partial x_2}{\partial \tau_j} = \frac{\sum_{n=0}^{4} \frac{\partial d_n}{\partial \tau_j} x_2^{\,n}}{\sum_{n=0}^{4} n d_n x_2^{\,n-1}} \tag{A1}$$

The expressions for $\partial d_n/\partial \tau_j$ for model A are given in table IV. The equations used in the computation of $\partial x_i/\partial \tau_j$ for air model A are as follows:

$$F_1 = \frac{2b_2 - \gamma_0 x_2 - \gamma_4 x_2^{\,2}}{b_2 + \gamma_1 x_2} \tag{A2}$$

$$\frac{\partial F_1}{\partial x_2} = -\frac{\gamma_0 + 2\gamma_4 x_2 + \gamma_1 x_1}{b_2 + \gamma_1 x_2} \tag{A3}$$

$$\left.\begin{aligned}
\frac{\partial x_1}{\partial \tau_1} &= \frac{\partial F_1}{\partial x_2}\frac{\partial x_2}{\partial \tau_1} && \text{(a)}\\
\frac{\partial x_1}{\partial \tau_2} &= \frac{\partial F_1}{\partial x_2}\frac{\partial x_2}{\partial \tau_2} - \frac{2(\gamma_0 - b_2)x_2^{\,2}}{b_2 + \gamma_1 x_2} && \text{(b)}\\
\frac{\partial x_1}{\partial \tau_3} &= \frac{\partial F_1}{\partial x_2}\frac{\partial x_2}{\partial \tau_3} - \frac{(\gamma_0 - b_2)x_1 x_2}{b_2 + \gamma_1 x_2} && \text{(c)}
\end{aligned}\right\} \tag{A4}$$

$$\left.\begin{aligned}
\frac{\partial x_4}{\partial \tau_1} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_1} + x_1^{\,2} && \text{(a)}\\
\frac{\partial x_4}{\partial \tau_2} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_2} && \text{(b)}\\
\frac{\partial x_4}{\partial \tau_3} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_3} && \text{(c)}
\end{aligned}\right\} \tag{A5}$$

$$\left.\begin{aligned}
\frac{\partial x_5}{\partial \tau_1} &= 2\tau_2 x_2 \frac{\partial x_2}{\partial \tau_1} && \text{(a)}\\
\frac{\partial x_5}{\partial \tau_2} &= 2\tau_2 x_2 \frac{\partial x_2}{\partial \tau_2} + x_2^{\,2} && \text{(b)}\\
\frac{\partial x_5}{\partial \tau_3} &= 2\tau_2 x_2 \frac{\partial x_2}{\partial \tau_3} && \text{(c)}
\end{aligned}\right\} \quad \text{(A6)}$$

$$\left.\begin{aligned}
\frac{\partial x_6}{\partial \tau_1} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_1} x_2 + x_1 \frac{\partial x_2}{\partial \tau_1}\right) && \text{(a)}\\
\frac{\partial x_6}{\partial \tau_2} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_2} x_2 + x_1 \frac{\partial x_2}{\partial \tau_2}\right) && \text{(b)}\\
\frac{\partial x_6}{\partial \tau_3} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_3} x_2 + x_1 \frac{\partial x_2}{\partial \tau_3}\right) + x_1 x_2 && \text{(c)}
\end{aligned}\right\} \quad \text{(A7)}$$

$$\frac{\partial x_3}{\partial \tau_j} = b_3\left(\frac{\partial x_1}{\partial \tau_j} + 2\,\frac{\partial x_4}{\partial \tau_j} + \frac{\partial x_6}{\partial \tau_j}\right) \quad \text{(A8)}$$

The equations for air model B are

$$\left.\begin{aligned}
\frac{\partial A}{\partial \tau_1} &= -a_2 x_1^{\,2}\alpha_2\beta_1 - \alpha_1\alpha_2 \frac{a_2 + 2b_2}{1 + b_2} x_1^{\,2} - 2\alpha_1\beta_1 a_2 x_1^{\,2} && \text{(a)}\\
\frac{\partial A}{\partial \tau_3} &= \alpha_1 a_2 x_1 \beta_1 + \alpha_1^{\,2} \frac{1 - a_2 - b_2}{1 + b_2} x_1 - \frac{1}{\tau_4} x_1^{\,2}\left(a_2 + \frac{1 - a_2 - b_2}{1 + b_2}\right) && \text{(b)}\\
\frac{\partial A}{\partial \tau_4} &= \frac{x_1}{\tau_4^{\,2}}\left(\alpha_2 + \beta_2\right) && \text{(c)}\\
\frac{\partial A}{\partial \tau_5} &= 0 && \text{(d)}\\
\frac{\partial B}{\partial \tau_1} &= -2a_2 x_1^{\,2}\alpha_2\left(\alpha_1\beta_1 - \frac{1}{\tau_4} x_1\right) - \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\left(a_2\beta_1 + \alpha_1 \frac{a_2 + 2b_2}{1 + b_2}\right) x_1^{\,2}\\
&\quad - 2\left(\alpha_1\beta_2 - \alpha_2\beta_1\right) a_2 x_1^{\,2}\alpha_1\\
&\quad + \left(\alpha_1^{\,2} - \frac{1}{\tau_4} x_1\right)\left(\alpha_2 \frac{a_2 + 2b_2}{1 + b_2} - a_2\beta_2\right) x_1^{\,2} && \text{(e)}
\end{aligned}\right\} \quad \text{(A9)}$$

(Equations continued on next page)

$$\left.\begin{aligned}
&\frac{\partial B}{\partial \tau_3} = 2\alpha_1 a_2 x_1\left(\alpha_1\beta_1 - \frac{1}{\tau_4}\right)x_1 + x_1\left(\alpha_1^2 - \frac{1}{\tau_4}x_1\right)\left(\alpha_1\frac{1 - a_2 - b_2}{1 + b_2} - a_2\beta_1\right) && \text{(f)}\\
&\frac{\partial B}{\partial \tau_4} = \left(2\alpha_1\alpha_2 + \alpha_1\beta_2 - \alpha_2\beta_1 + \frac{1}{\tau_5}\right)\frac{x_1}{\tau_4^2} && \text{(g)}\\
&\frac{\partial B}{\partial \tau_5} = -\frac{1}{\tau_5^2}\left(\alpha_1\beta_1 - \frac{1}{\tau_4}x_1\right) && \text{(h)}\\
&\frac{\partial\left(D/\alpha_2\right)}{\partial \tau_1} = -x_1^2\alpha_2\left(a_2\beta_2 + \alpha_2\frac{a_2 + 2b_2}{1 + b_2}\right) && \text{(i)}\\
&\frac{\partial\left(D/\alpha_2\right)}{\partial \tau_3} = 2\alpha_1 a_2\beta_1 x_1 + \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\frac{1 - a_2 - b_2}{1 + b_2}x_1\\
&\qquad - \left(\alpha_1\frac{1 - a_2 - b_2}{1 + b_2} - a_2\beta_1\right)\alpha_2 x_1 - \left(\alpha_1\beta_2 - \alpha_2\beta_1\right)a_2 x_1 && \text{(j)}\\
&\frac{\partial\left(D/\alpha_2\right)}{\partial \tau_4} = 0 && \text{(k)}\\
&\frac{\partial\left(D/\alpha_2\right)}{\partial \tau_5} = -\frac{\beta_2}{\tau_5^2} && \text{(l)}
\end{aligned}\right\} \text{(A9)}$$

$$\left.\begin{aligned}
&\frac{\partial \alpha_1}{\partial x_1} = -a_1 - 2a_2\tau_1 x_1 && \text{(a)}\\
&\frac{\partial \alpha_2}{\partial x_1} = a_2\tau_3 && \text{(b)}\\
&\frac{\partial \beta_1}{\partial x_1} = -\frac{a_1 + b_2}{1 + b2} - \frac{2\left(a_2 + 2b_2\right)\tau_1}{1 + b2}x_1 && \text{(c)}\\
&\frac{\partial \beta_2}{\partial x_1} = \frac{1 - a_2 - b_2}{1 + b_2}\tau_3 && \text{(d)}
\end{aligned}\right\} \text{(A10)}$$

$$\left.\begin{aligned}
\frac{\partial A}{\partial x_1} &= \frac{\partial \alpha_1}{\partial x_1}\alpha_2\beta_1 + \alpha_1\frac{\partial \alpha_2}{\partial x_1}\beta_1 + \alpha_1\alpha_2\frac{\partial \beta_1}{\partial x_1} + 2\alpha_1\frac{\partial \alpha_1}{\partial x_1}\beta_2 + \alpha_1^{\,2}\frac{\partial \beta_2}{\partial x_1} - \frac{1}{\tau_4}\left(\alpha_2 + \beta_2\right) \\
&\quad - \frac{x_1}{\tau_4}\left(\frac{\partial \alpha_2}{\partial x_1} + \frac{\partial \beta_2}{\partial x_1}\right) && \text{(a)} \\
\frac{\partial B}{\partial x_1} &= 2\left(\frac{\partial \alpha_1}{\partial x_1}\alpha_2 + \alpha_1\frac{\partial \alpha_2}{\partial x_1}\right)\left(\alpha_1\beta_1 - \frac{1}{\tau_4}x_1\right) + \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\left(\frac{\partial \alpha_1}{\partial x_1}\beta_1\right. \\
&\quad \left. + \alpha_1\frac{\partial \beta_1}{\partial x_1} - \frac{1}{\tau_4}\right) + \left(\frac{\partial \alpha_1}{\partial x_1}\beta_2 + \alpha_1\frac{\partial \beta_2}{\partial x_1} - \frac{\partial \alpha_2}{\partial x_1}\beta_1 - \alpha_2\frac{\partial \beta_1}{\partial x_1}\right)\left(\alpha_1^{\,2} - \frac{1}{\tau_4}x_1\right) \\
&\quad + \left(\alpha_1\beta_2 - \alpha_2\beta_1\right)\left(2\alpha_1\frac{\partial \alpha_1}{\partial x_1} - \frac{1}{\tau_4}\right) && \text{(b)} \\
\frac{\partial\left(D/\alpha_2\right)}{\partial x_1} &= 2\left(\frac{\partial \alpha_1}{\partial x_1}\alpha_2 + \alpha_1\frac{\partial \alpha_2}{\partial x_1}\right)\beta_2 + \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\frac{\partial \beta_2}{\partial x_1} - \left(\frac{\partial \alpha_1}{\partial x_1}\beta_2 + \alpha_1\frac{\partial \beta_2}{\partial x_1}\right. \\
&\quad \left. - \frac{\partial \alpha_2}{\partial x_1}\beta_1 - \alpha_2\frac{\partial \beta_1}{\partial x_1}\right)\alpha_2 - \left(\alpha_1\beta_2 - \alpha_2\beta_1\right)\frac{\partial \alpha_2}{\partial x_1} && \text{(c)}
\end{aligned}\right\}\quad \text{(A11)}$$

$$\left.\begin{aligned}
&\frac{\partial \alpha_2}{\partial \tau_3} = a_2 x_1 && && \text{(a)} \\
&\frac{\partial \alpha_2}{\partial \tau_j} = 0 && (\text{for} \quad j \neq 3) && \text{(b)} \\
&\frac{\partial F}{\partial \tau_j} = \frac{\partial\left(D/\alpha_2\right)}{\partial \tau_j}B + \frac{D}{\alpha_2}\frac{\partial B}{\partial \tau_j} - \frac{\partial \alpha_2}{\partial \tau_j}A^2 - 2\alpha_2 A\frac{\partial A}{\partial \tau_j} && && \text{(c)} \\
&\frac{\partial F}{\partial x_1} = \frac{\partial\left(D/\alpha_2\right)}{\partial x_1}B + \frac{D}{\alpha_2}\frac{\partial B}{\partial x_1} - \frac{\partial \alpha_2}{\partial x_1}A^2 - 2\alpha_2 A\frac{\partial A}{\partial x_1} && && \text{(d)}
\end{aligned}\right\}\quad \text{(A12)}$$

$$\frac{\partial x_1}{\partial \tau_j} = -\frac{\partial F/\partial \tau_j}{\partial F/\partial x_1} \qquad \text{(A13)}$$

$$\frac{\partial x_2}{\partial \tau_j} = \frac{\frac{\partial A}{\partial \tau_j} + \frac{\partial A}{\partial x_1}\frac{\partial x_1}{\partial \tau_j}}{D/\alpha_2} - \left[\frac{\partial\left(D/\alpha_2\right)}{\partial \tau_j} + \frac{\partial\left(D/\alpha_2\right)}{\partial x_1}\frac{\partial x_1}{\partial \tau_j}\right]\frac{x_2}{D/\alpha_2} \tag{A14}$$

$$\left.\begin{aligned}
\frac{\partial x_7}{\partial \tau_1} &= \frac{\partial \alpha_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_1} - \alpha_2\frac{\partial x_2}{\partial \tau_1} - \frac{\partial \alpha_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_1}x_2 - a_2 x_1{}^2 && \text{(a)}\\
\frac{\partial x_7}{\partial \tau_3} &= \frac{\partial \alpha_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_3} - \alpha_2\frac{\partial x_2}{\partial \tau_3} - \frac{\partial \alpha_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_3}x_2 - a_2 x_1 x_2 && \text{(b)}\\
\frac{\partial x_7}{\partial \tau_4} &= \frac{\partial \alpha_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_4} - \alpha_2\frac{\partial x_2}{\partial \tau_4} - \frac{\partial \alpha_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_4}x_2 && \text{(c)}\\
\frac{\partial x_7}{\partial \tau_5} &= \frac{\partial \alpha_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_5} - \alpha_2\frac{\partial x_2}{\partial \tau_5} - \frac{\partial \alpha_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_5}x_2 && \text{(d)}
\end{aligned}\right\} \tag{A15}$$

$$\left.\begin{aligned}
\frac{\partial x_8}{\partial \tau_1} &= \frac{\partial \beta_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_1} + \beta_2\frac{\partial x_2}{\partial \tau_1} + \frac{\partial \beta_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_1} - \frac{a_2 + 2b_2}{1 + b_2}x_1{}^2 && \text{(a)}\\
\frac{\partial x_8}{\partial \tau_3} &= \frac{\partial \beta_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_3} + \beta_2\frac{\partial x_2}{\partial \tau_3} + \frac{\partial \beta_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_3} + \frac{1 - a_2 - b_2}{1 + b_2}x_1 x_2 && \text{(b)}\\
\frac{\partial x_8}{\partial \tau_4} &= \frac{\partial \beta_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_4} + \beta_2\frac{\partial x_2}{\partial \tau_4} + \frac{\partial \beta_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_4} && \text{(c)}\\
\frac{\partial x_8}{\partial \tau_5} &= \frac{\partial \beta_1}{\partial x_1}\frac{\partial x_1}{\partial \tau_5} + \beta_2\frac{\partial x_2}{\partial \tau_5} + \frac{\partial \beta_2}{\partial x_1}\frac{\partial x_1}{\partial \tau_5} && \text{(d)}
\end{aligned}\right\} \tag{A16}$$

$$\frac{\partial x_9}{\partial \tau_j} = \frac{\partial x_7}{\partial \tau_j} - \frac{\partial x_8}{\partial \tau_j} \tag{A17}$$

$$\left.\begin{aligned}
\frac{\partial x_4}{\partial \tau_1} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_1} + x_1^2 && \text{(a)}\\
\frac{\partial x_4}{\partial \tau_3} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_3} && \text{(b)}\\
\frac{\partial x_4}{\partial \tau_4} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_4} && \text{(c)}\\
\frac{\partial x_4}{\partial \tau_5} &= 2\tau_1 x_1 \frac{\partial x_1}{\partial \tau_5} && \text{(d)}
\end{aligned}\right\} \tag{A18}$$

$$\left.\begin{aligned}
\frac{\partial x_6}{\partial \tau_1} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_1} x_2 + x_1 \frac{\partial x_2}{\partial \tau_1}\right) && \text{(a)}\\
\frac{\partial x_6}{\partial \tau_3} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_3} x_2 + x_1 \frac{\partial x_2}{\partial \tau_3}\right) + x_1 x_2 && \text{(b)}\\
\frac{\partial x_6}{\partial \tau_4} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_4} x_2 + x_1 \frac{\partial x_2}{\partial \tau_4}\right) && \text{(c)}\\
\frac{\partial x_6}{\partial \tau_5} &= \tau_3\left(\frac{\partial x_1}{\partial \tau_5} x_2 + x_1 \frac{\partial x_2}{\partial \tau_5}\right) && \text{(d)}
\end{aligned}\right\} \tag{A19}$$

$$\frac{\partial x_3}{\partial \tau_j} = b_3\left(\frac{\partial x_1}{\partial \tau_j} + \frac{\partial x_8}{\partial \tau_j} + 2\,\frac{\partial x_4}{\partial \tau_j} + \frac{\partial x_6}{\partial \tau_j}\right) \tag{A20}$$

For model C,

$$\frac{\partial x_7}{\partial \tau_j} = -\frac{\displaystyle\sum_{n=0}^{4} \frac{\partial d_n}{\partial \tau_j} x_7^{\,n}}{\displaystyle\sum_{n=0}^{4} n d_n x_7^{\,n-1}} \tag{A21}$$

The expressions for $\partial d_n/\partial \tau_j$ for model C are given in table V. The equations used in the computation of $\partial x_i/\partial \tau_j$ for air model C are as follows:

$$F_8 = 1 + b_2 \frac{1 + \tau_4 x_7}{1 + \tau_5 x_7} + b_3 \frac{1 + \tau_4 x_7}{1 + \tau_6 x_7} \tag{A22}$$

$$\left.\begin{aligned}
&\frac{\partial F_8}{\partial x_7} = \tau_4\left(\frac{b_2}{1 + \tau_5 x_7} + \frac{b_3}{1 + \tau_6 x_7}\right) - \left(1 + \tau_4 x_7\right)\left[\frac{\tau_5 b_2}{\left(1 + \tau_5 x_7\right)^2} + \frac{\tau_6 b_3}{\left(1 + \tau_6 x_7\right)^2}\right] && \text{(a)}\\
&\frac{\partial F_8}{\partial \tau_4} = x_7\left(\frac{b_2}{1 + \tau_5 x_7} + \frac{b_3}{1 + \tau_6 x_7}\right) && \text{(b)}\\
&\frac{\partial F_8}{\partial \tau_5} = - \frac{1 + \tau_4 x_7}{\left(1 + \tau_5 x_7\right)^2} b_2 x_7 && \text{(c)}\\
&\frac{\partial F_8}{\partial \tau_6} = - \frac{1 + \tau_4 x_7}{\left(1 + \tau_6 x_7\right)^2} b_3 x_7 && \text{(d)}
\end{aligned}\right\} \text{(A23)}$$

$$\frac{\partial x_8}{\partial \tau_j} = \frac{1}{F_8}\left(1 - x_8 \frac{\partial F_8}{\partial x_7}\right)\frac{\partial x_7}{\partial \tau_j} - \frac{x_8}{F_8} \frac{\partial F_8}{\partial \tau_j} \tag{A24}$$

$$\left.\begin{aligned}
&\frac{\partial x_1}{\partial \tau_4} = \tau_4\left(\frac{\partial x_8}{\partial \tau_4} x_7 + x_8 \frac{\partial x_7}{\partial \tau_4}\right) + x_8 x_7 && \text{(a)}\\
&\frac{\partial x_1}{\partial \tau_5} = \tau_4\left(\frac{\partial x_8}{\partial \tau_5} x_7 + x_8 \frac{\partial x_7}{\partial \tau_5}\right) && \text{(b)}\\
&\frac{\partial x_1}{\partial \tau_6} = \tau_4\left(\frac{\partial x_8}{\partial \tau_6} x_7 + x_8 \frac{\partial x_7}{\partial \tau_6}\right) && \text{(c)}
\end{aligned}\right\} \text{(A25)}$$

$$\left.\begin{aligned}
&\frac{\partial x_9}{\partial x_7} = \frac{b_2 \tau_4 x_8 - \tau_5 x_9}{1 + \tau_5 x_7} && \text{(a)}\\
&\frac{\partial x_9}{\partial \tau_4} = \frac{\partial x_9}{\partial x_7} \frac{\partial x_7}{\partial \tau_4} + \frac{x_9}{x_8} \frac{\partial x_8}{\partial \tau_4} + \frac{b_2 x_7 x_8}{1 + \tau_4 x_7} && \text{(b)}\\
&\frac{\partial x_9}{\partial \tau_5} = \frac{\partial x_9}{\partial x_7} \frac{\partial x_7}{\partial \tau_5} + \frac{x_9}{x_8} \frac{\partial x_8}{\partial \tau_5} - \frac{x_7 x_9}{1 + \tau_4 x_7} && \text{(c)}\\
&\frac{\partial x_9}{\partial \tau_6} = \frac{\partial x_9}{\partial x_7} \frac{\partial x_7}{\partial \tau_6} + \frac{x_9}{x_8} \frac{\partial x_8}{\partial \tau_6} && \text{(d)}
\end{aligned}\right\} \text{(A26)}$$

$$\left.\begin{aligned}
&\frac{\partial x_{10}}{\partial x_7} = \frac{b_3\tau_4 x_8 - \tau_6 x_{10}}{1 + \tau_6 x_7} && \text{(a)}\\
&\frac{\partial x_{10}}{\partial \tau_4} = \frac{\partial x_{10}}{\partial x_7}\frac{\partial x_7}{\partial \tau_4} + \frac{x_{10}}{x_8}\frac{\partial x_8}{\partial \tau_4} + \frac{b_3 x_7 x_8}{1 + \tau_6 x_7} && \text{(b)}\\
&\frac{\partial x_{10}}{\partial \tau_5} = \frac{\partial x_{10}}{\partial x_7}\frac{\partial x_7}{\partial \tau_5} + \frac{x_{10}}{x_8}\frac{\partial x_8}{\partial \tau_5} && \text{(c)}\\
&\frac{\partial x_{10}}{\partial \tau_6} = \frac{\partial x_{10}}{\partial x_7}\frac{\partial x_7}{\partial \tau_6} + \frac{x_{10}}{x_8}\frac{\partial x_8}{\partial \tau_6} - \frac{x_7 x_{10}}{1 + \tau_6 x_7} && \text{(d)}
\end{aligned}\right\} \quad \text{(A27)}$$

$$\left.\begin{aligned}
&\frac{\partial x_3}{\partial \tau_4} = \tau_6\left(\frac{\partial x_7}{\partial \tau_4} x_{10} + x_7 \frac{\partial x_{10}}{\partial \tau_4}\right) && \text{(a)}\\
&\frac{\partial x_3}{\partial \tau_5} = \tau_6\left(\frac{\partial x_7}{\partial \tau_5} x_{10} + x_7 \frac{\partial x_{10}}{\partial \tau_5}\right) && \text{(b)}\\
&\frac{\partial x_3}{\partial \tau_6} = \tau_6\left(\frac{\partial x_7}{\partial \tau_6} x_{10} + x_7 \frac{\partial x_{10}}{\partial \tau_6}\right) + x_7 x_{10} && \text{(c)}
\end{aligned}\right\} \quad \text{(A28)}$$

$$\left.\begin{aligned}
&\frac{\partial x_2}{\partial \tau_4} = \tau_5\left(\frac{\partial x_9}{\partial \tau_4} x_7 + x_9 \frac{\partial x_7}{\partial \tau_4}\right) && \text{(a)}\\
&\frac{\partial x_2}{\partial \tau_5} = \tau_5\left(\frac{\partial x_9}{\partial \tau_5} x_7 + x_9 \frac{\partial x_7}{\partial \tau_5}\right) + x_7 x_9 && \text{(b)}\\
&\frac{\partial x_2}{\partial \tau_6} = \tau_5\left(\frac{\partial x_9}{\partial \tau_6} x_7 + x_9 \frac{\partial x_7}{\partial \tau_6}\right) && \text{(c)}
\end{aligned}\right\} \quad \text{(A29)}$$

For model D,

$$\frac{\partial x_7}{\partial \tau_j} = - \frac{\sum_{n=0}^{4} \frac{\partial d_n}{\partial \tau_j} x_7{}^n}{\sum_{n=0}^{4} n d_n x_7{}^{n-1}} \tag{A30}$$

APPENDIX A

The expressions for $\partial d_n/\partial \tau_j$ for model D are given in table VI. The equations used in the computation of $\partial x_i/\partial \tau_j$ for air model D are

$$F_{11} = 1 + \left(1 + \tau_7 x_7\right)\left(1 + b_2 + b_3\right) + \left(1 + \tau_7 x_7\right)\left(\frac{b_2}{1 + \tau_x x_7} + \frac{b_3}{1 + \tau_9 x_7}\right) \tag{A31}$$

$$\left.\begin{aligned}
\frac{\partial F_{11}}{\partial x_7} &= \tau_7\left(1 + b_2 + b_3 + \frac{b_2}{1 + \tau_8 x_7} + \frac{b_3}{1 + \tau_9 x_7}\right) \\
&\quad - \left(1 + \tau_7 x_7\right)\left[\frac{b_2 \tau_8}{\left(1 + \tau_8 x_7\right)^2} + \frac{b_3 \tau_9}{\left(1 + \tau_9 x_7\right)^2}\right] && \text{(a)} \\
\frac{\partial F_{11}}{\partial \tau_7} &= x_7\left[1 + b_2\left(1 + \frac{1}{1 + \tau_8 x_7}\right) + b_3\left(1 + \frac{1}{1 + \tau_9 x_7}\right)\right] + \frac{\partial F_{11}}{\partial x_7}\,\frac{\partial x_7}{\partial \tau_7} && \text{(b)} \\
\frac{\partial F_{11}}{\partial \tau_8} &= -\, b_2 x_7 \frac{1 + \tau_7 x_7}{\left(1 + \tau_8 x_7\right)^2} + \frac{\partial F_{11}}{\partial x_7}\,\frac{\partial x_7}{\partial \tau_8} && \text{(c)} \\
\frac{\partial F_{11}}{\partial \tau_9} &= -b_3 x_7 \frac{1 + \tau_7 x_7}{\left(1 + \tau_9 x_7\right)^2} + \frac{\partial F_{11}}{\partial x_7}\,\frac{\partial x_7}{\partial \tau_9} && \text{(d)}
\end{aligned}\right\} \tag{A32}$$

$$\frac{\partial x_{11}}{\partial \tau_j} = \frac{1}{F_{11}}\left(1 - x_{11}\frac{\partial F_{11}}{\partial x_7}\right)\frac{\partial x_7}{\partial \tau_j} - \frac{x_{11}}{F_{11}}\,\frac{\partial F_{11}}{\partial \tau_j} \tag{A33}$$

$$\left.\begin{aligned}
\frac{\partial x_8}{\partial \tau_7} &= \tau_7 \frac{\partial x_7}{\partial \tau_7} x_{11} + \tau_7 x_7 \frac{\partial x_{11}}{\partial \tau_7} + x_7 x_{11} && \text{(a)} \\
\frac{\partial x_8}{\partial \tau_8} &= \tau_7 \frac{\partial x_7}{\partial \tau_8} x_{11} + \tau_7 x_7 \frac{\partial x_{11}}{\partial \tau_8} && \text{(b)} \\
\frac{\partial x_8}{\partial \tau_9} &= \tau_7 \frac{\partial x_7}{\partial \tau_9} x_{11} + \tau_7 x_7 \frac{\partial x_{11}}{\partial \tau_9} && \text{(c)}
\end{aligned}\right\} \tag{A34}$$

$$
\left.
\begin{aligned}
&\frac{\partial x_{13}}{\partial x_7} = \frac{b_3 \tau_7 x_{11} - \tau_9 x_{13}}{1 + \tau_9 x_7} && \text{(a)}\\
&\frac{\partial x_{13}}{\partial \tau_7} = \frac{\partial x_{13}}{\partial x_7}\frac{\partial x_7}{\partial \tau_7} + \frac{x_{13}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_7} + \frac{b_3 x_7 x_{11}}{1 + \tau_9 x_7} && \text{(b)}\\
&\frac{\partial x_{13}}{\partial \tau_8} = \frac{\partial x_{13}}{\partial x_7}\frac{\partial x_7}{\partial \tau_8} + \frac{x_{13}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_8} && \text{(c)}\\
&\frac{\partial x_{13}}{\partial \tau_9} = \frac{\partial x_{13}}{\partial x_7}\frac{\partial x_7}{\partial \tau_9} + \frac{x_{13}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_9} - \frac{x_7 x_{13}}{1 + \tau_9 x_7} && \text{(d)}
\end{aligned}
\right\} \quad \text{(A35)}
$$

$$
\left.
\begin{aligned}
&\frac{\partial x_{10}}{\partial \tau_7} = \tau_9 \frac{\partial x_7}{\partial \tau_7} x_{13} + \tau_9 x_7 \frac{\partial x_{13}}{\partial \tau_7} && \text{(a)}\\
&\frac{\partial x_{10}}{\partial \tau_8} = \tau_9 \frac{\partial x_7}{\partial \tau_8} x_{13} + \tau_9 x_7 \frac{\partial x_{13}}{\partial \tau_8} && \text{(b)}\\
&\frac{\partial x_{10}}{\partial \tau_9} = \tau_9 \frac{\partial x_7}{\partial \tau_9} x_{13} + \tau_9 x_7 \frac{\partial x_{13}}{\partial \tau_9} + x_7 x_{13} && \text{(c)}
\end{aligned}
\right\} \quad \text{(A36)}
$$

$$
\left.
\begin{aligned}
&\frac{\partial x_{12}}{\partial x_7} = \frac{b_2 \tau_7 x_{11} - \tau_8 x_{12}}{1 + \tau_8 x_7} && \text{(a)}\\
&\frac{\partial x_{12}}{\partial \tau_7} = \frac{\partial x_{12}}{\partial x_7}\frac{\partial x_7}{\partial \tau_7} + \frac{x_{12}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_7} + \frac{b_2 x_7 x_{11}}{1 + \tau_8 x_7} && \text{(b)}\\
&\frac{\partial x_{12}}{\partial \tau_8} = \frac{\partial x_{12}}{\partial x_7}\frac{\partial x_7}{\partial \tau_8} + \frac{x_{12}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_8} - \frac{x_7 x_{12}}{1 + \tau_8 x_7} && \text{(c)}\\
&\frac{\partial x_{12}}{\partial \tau_9} = \frac{\partial x_{12}}{\partial x_7}\frac{\partial x_7}{\partial \tau_9} + \frac{x_{12}}{x_{11}}\frac{\partial x_{11}}{\partial \tau_9} && \text{(d)}
\end{aligned}
\right\} \quad \text{(A37)}
$$

$$\left.\begin{aligned}
\frac{\partial x_9}{\partial \tau_7} &= \tau_8\left(\frac{\partial x_7}{\partial \tau_7}\, x_{12} + x_7\, \frac{\partial x_{12}}{\partial \tau_7}\right) && \text{(a)}\\
\frac{\partial x_9}{\partial \tau_8} &= \tau_8\left(\frac{\partial x_7}{\partial \tau_8}\, x_{12} + x_7\, \frac{\partial x_{12}}{\partial \tau_8}\right) + x_7 x_{12} && \text{(b)}\\
\frac{\partial x_9}{\partial \tau_9} &= \tau_8\left(\frac{\partial x_7}{\partial \tau_9}\, x_{12} + x_7\, \frac{\partial x_{12}}{\partial \tau_9}\right) && \text{(c)}
\end{aligned}\right\} \quad \text{(A38)}$$

APPENDIX B

EQUATIONS FOR COMPUTING $\dfrac{\partial x_i}{\partial b_k}$

The equations are presented in the order required for computation for each model. The following equations are used in the computation of $\partial x_i/\partial b_k$ for air model A:

$$\frac{\partial d_0}{\partial b_2} = 2\,\frac{d_0}{b_2}$$

$$\frac{\partial d_0}{\partial b_3} = 0$$

$$\frac{\partial d_1}{\partial b_2} = \frac{d_1}{b_2} - b_2\left(1 + 8\tau_1\right)$$

$$\frac{\partial d_1}{\partial b_3} = -b_2\left(1 + 8\tau_1 - 2\tau_3\right)$$

$$\frac{\partial d_2}{\partial b_2} = 4\tau_1\left[2\left(b_2\tau_2 - \gamma_0\tau_1\right) + 2b_2\left(\tau_2 - 2\tau_1\right) + \gamma_0\right] - \gamma_3 - b_2\left(\tau_2 + \tau_3\right)$$
$$- \tau_3\gamma_2 - \gamma_1\left(1 + \tau_3\right)$$

$$\frac{\partial d_2}{\partial b_3} = 4\tau_1\left(\gamma_0 - 4b_2\tau_1\right) - b_2\left(2\tau_2 + \tau_3\right) - 2\tau_3\gamma_2 - \gamma_1$$

$$\frac{\partial d_3}{\partial b_2} = -8\tau_1\left(b_2\tau_2 - \gamma_0\tau_1\right) - 4\tau_1\gamma_0\left(\tau_2 - 2\tau_1\right) - \tau_2\gamma_1 - b_2\tau_2\tau_3$$
$$- \tau_3\gamma_3 - \gamma_1\left(2\tau_2 + \tau_3\right)$$

$$\frac{\partial d_3}{\partial b_3} = -8\tau_1\tau_2 b_2 - 2b_2\tau_2\tau_3 - 2\tau_3\gamma_3 - \gamma_1\left(2\tau_2 + \tau_3\right)$$

$$\frac{\partial d_4}{\partial b_2} = 8\tau_1\left(b_2\tau_2 - \gamma_0\tau_1\right)\left(\tau_2 - 2\tau_1\right) - 2\tau_2\tau_3\gamma_1$$

$$\frac{\partial d_4}{\partial b_3} = 16\tau_1\left(b_2\tau_2 - \gamma_0\tau_1\right)$$

$$\frac{\partial x_2}{\partial b_k} = - \frac{\sum_{n=0}^{4} \frac{\partial d_n}{\partial b_k} x_2^n}{\sum_{n=0}^{4} n d_n x_2^{n-1}}$$

$\partial F_1/\partial x_2$ is computed from equation (A2).

$$\frac{\partial x_1}{\partial b_2} = \frac{\partial F_1}{\partial x_2}\frac{\partial x_2}{\partial b_2} + 2\,\frac{1 - x_2 - \tau_2 x_2^2}{b_2 + \gamma_1 x_2} - x_1\,\frac{1 + \tau_3 x_2}{b_2 + \gamma_1 x_2}$$

$$\frac{\partial x_1}{\partial b_3} = \frac{\partial F_1}{\partial x_2}\frac{\partial x_2}{\partial b_3} - 2\,\frac{x_2 + 2\tau_2 x_2^2}{b_2 + \gamma_1 x_2} - \frac{2\tau_3 x_1 x_2}{b_2 + \gamma_1 x_2}$$

$$\frac{\partial x_4}{\partial b_k} = 2\tau_1 x_1 \frac{\partial x_1}{\partial b_k}$$

$$\frac{\partial x_5}{\partial b_k} = 2\tau_2 x_2 \frac{\partial x_2}{\partial b_k}$$

$$\frac{\partial x_6}{\partial b_k} = \tau_3\left(\frac{\partial x_1}{\partial b_k} x_2 + x_1 \frac{\partial x_2}{\partial b_k}\right)$$

$$\frac{\partial x_3}{\partial b_2} = b_3\left(\frac{\partial x_1}{\partial b_2} + 2\,\frac{\partial x_4}{\partial b_2} + \frac{\partial x_6}{\partial b_2}\right)$$

$$\frac{\partial x_3}{\partial b_3} = b_3\left(\frac{\partial x_1}{\partial b_3} + 2\,\frac{\partial x_4}{\partial b_3} + \frac{\partial x_6}{\partial b_3}\right) + x_1 + 2x_4 + x_6$$

The equations for air model B are

$$\frac{\partial a_0}{\partial b_2} = \frac{a_0^2 b_3}{\left(1 + b_2\right)^2}$$

$$\frac{\partial a_0}{\partial b_3} = - \frac{a_0^2}{1 + b_2}$$

APPENDIX B

$$\frac{\partial a_1}{\partial b_2} = \frac{\partial a_0}{\partial b_2}\left(1 + \frac{b_3}{1 + b_2}\right) - \frac{a_0 b_3}{\left(1 + b_2\right)^2}$$

$$\frac{\partial a_1}{\partial b_3} = \frac{\partial a_0}{\partial b_3}\left(1 + \frac{b_3}{1 + b_2}\right) + \frac{a_0}{1 + b_2}$$

$$\frac{\partial a_2}{\partial b_2} = \frac{\partial a_0}{\partial b_2}\left(1 + \frac{2b_3}{1 + b_2}\right) - \frac{2a_0 b_3}{\left(1 + b_2\right)^2}$$

$$\frac{\partial a_2}{\partial b_3} = \frac{\partial a_0}{\partial b_3}\left(1 + \frac{2b_3}{1 + b_2}\right) + \frac{2a_0}{1 + b_2}$$

$$\frac{\partial \alpha_1}{\partial b_k} = \frac{\partial a_0}{\partial b_k} - \frac{\partial a_1}{\partial b_k} x_1 - \frac{\partial a_2}{\partial b_k} \tau_1 x_1^2$$

$$\frac{\partial \alpha_2}{\partial b_k} = \frac{\partial a_1}{\partial b_k} + \frac{\partial a_2}{\partial b_k} \tau_3 x_1$$

$$\frac{\partial \beta_1}{\partial b_2} = \left(1 + b_2\right)^{-1}\left[\frac{\partial a_0}{\partial b_2} - \left(\frac{\partial a_1}{\partial b_2} + 1\right)x_1 - \left(\frac{\partial a_2}{\partial b_2} + 2\right)\tau_1 x_1^2\right] - \frac{\beta_1}{1 + b_2}$$

$$\frac{\partial \beta_1}{\partial b_3} = \left(1 + b_2\right)^{-1}\left(\frac{\partial a_0}{\partial b_3} - \frac{\partial a_1}{\partial b_3} x_1 - \frac{\partial a_2}{\partial b_3} \tau_1 x_1^2\right)$$

$$\frac{\partial \beta_2}{\partial b_2} = -\left(1 + b_2\right)^{-1}\left[\frac{\partial a_1}{\partial b_2} + \left(\frac{\partial a_2}{\partial b_2} + 1\right)\tau_3 x_1\right] - \frac{\beta_2}{1 + b_2}$$

$$\frac{\partial \beta_2}{\partial b_3} = -\left(1 + b_2\right)^{-1}\left(\frac{\partial a_1}{\partial b_3} + \frac{\partial a_2}{\partial b_3} \tau_3 x_1\right)$$

$$\frac{\partial A}{\partial b_k} = \frac{\partial \alpha_1}{\partial b_k}\left(\alpha_2 \beta_1 + 2\alpha_1 \beta_2\right) + \alpha_1 \beta_1 \frac{\partial \alpha_2}{\partial b_k} + \alpha_1 \alpha_2 \frac{\partial \beta_1}{\partial b_k} + \alpha_1^2 \frac{\partial \beta_2}{\partial b_k} - \frac{1}{\tau_4} x_1\left(\frac{\partial \alpha_2}{\partial b_k} + \frac{\partial \beta_2}{\partial b_k}\right)$$

$$\frac{\partial B}{\partial b_k} = 2\left(\frac{\partial \alpha_1}{\partial b_k} \alpha_2 + \alpha_1 \frac{\partial \alpha_2}{\partial b_k}\right)\left(\alpha_1 \beta_1 - \frac{1}{\tau_4} x_1\right) + \left(\frac{\partial \alpha_1}{\partial b_k} \beta_2 + \alpha_1 \frac{\partial \beta_2}{\partial b_k} - \frac{\partial \alpha_2}{\partial b_k} \beta_1\right.$$

$$\left. - \alpha_2 \frac{\partial \beta_1}{\partial b_k}\right)\left(\alpha_1^2 - \frac{1}{\tau_4} x_1\right) + \left(2\alpha_1 \alpha_2 + \frac{1}{\tau_5}\right)\left(\frac{\partial \alpha_1}{\partial b_k} \beta_1 + \alpha_1 \frac{\partial \beta_1}{\partial b_k}\right) + \left(\alpha_1 \beta_2 - \alpha_2 \beta_1\right) 2\alpha_1 \frac{\partial \alpha_1}{\partial b_k}$$

$$\frac{\partial(D/\alpha_2)}{\partial b_k} = 2\left(\frac{\partial\alpha_1}{\partial b_k}\alpha_2 + \alpha_1\frac{\partial\alpha_2}{\partial b_k}\right)\beta_2 + \left(2\alpha_1\alpha_2 + \frac{1}{\tau_5}\right)\frac{\partial\beta}{\partial b_k} - \left(\frac{\partial\alpha_1}{\partial b_k}\beta_2 + \alpha_1\frac{\partial\beta_2}{\partial b_k}\right.$$

$$\left. - \frac{\partial\alpha_2}{\partial b_k}\beta_1 - \alpha_2\frac{\partial\beta_1}{\partial b_k}\right)\alpha_2 - \left(\alpha_1\beta_2 - \alpha_2\beta_1\right)\frac{\partial\alpha_2}{\partial b_k}$$

$$\frac{\partial F}{\partial b_k} = \frac{\partial(D/\alpha_2)}{\partial b_k}B + \left(\frac{D}{\alpha_2}\right)\frac{\partial B}{\partial b_k} - \frac{\partial\alpha_2}{\partial b_k}A^2 - 2\alpha_2 A\frac{\partial A}{\partial b_k}$$

$\partial F/\partial x_1$ is obtained from equation (A12(d)).

$$\frac{\partial x_1}{\partial b_k} = -\frac{\partial F/\partial b_k}{\partial F/\partial x_1}$$

$$\frac{\partial x_2}{\partial b_k} = \frac{1}{D/\alpha_2}\left[\frac{\partial A}{\partial b_k} - x_2\frac{\partial(D/\alpha_2)}{\partial b_k}\right] + \frac{1}{D/\alpha_2}\frac{\partial x_1}{\partial b_k}\left[\frac{\partial A}{\partial x_1} - x_2\frac{\partial(D/\alpha_2)}{\partial x_1}\right]$$

$$\frac{\partial x_7}{\partial b_k} = \frac{\partial\alpha_1}{\partial b_k} - \frac{\partial\alpha_2}{\partial b_k}x_2 - \alpha_2\frac{\partial x_2}{\partial b_k} + \left(\frac{\partial\alpha_1}{\partial x_1} - \frac{\partial\alpha_2}{\partial x_1}x_2\right)\frac{\partial x_1}{\partial b_k}$$

$$\frac{\partial x_8}{\partial b_k} = \frac{\partial\beta_1}{\partial b_k} + \frac{\partial\beta_2}{\partial b_k}x_2 + \beta_2\frac{\partial x_2}{\partial b_k} + \left(\frac{\partial\beta_1}{\partial x_1} + \frac{\partial\beta_2}{\partial x_1}x_2\right)\frac{\partial x_1}{\partial b_k}$$

$$\frac{\partial x_9}{\partial b_k} = \frac{\partial x_7}{\partial b_k} - \frac{\partial x_8}{\partial b_k}$$

$$\frac{\partial x_4}{\partial b_k} = 2\tau_1 x_1\frac{\partial x_1}{\partial b_k}$$

$$\frac{\partial x_6}{\partial b_k} = \tau_3\left(\frac{\partial x_1}{\partial b_k}x_2 + x_1\frac{\partial x_2}{\partial b_k}\right)$$

$$\frac{\partial x_3}{\partial b_2} = b_3\left(\frac{\partial x_1}{\partial b_2} + \frac{\partial x_8}{\partial b_2} + 2\frac{\partial x_4}{\partial b_2} + \frac{\partial x_6}{\partial b_2}\right)$$

$$\frac{\partial x_3}{\partial b_3} = b_3\left(\frac{\partial x_1}{\partial b_3} + \frac{\partial x_8}{\partial b_3} + 2\frac{\partial x_4}{\partial b_3} + \frac{\partial x_6}{\partial b_3}\right) + \left(x_1 + x_8 + 2x_4 + x_6\right)$$

APPENDIX B

The equations for air model C are

$$\frac{\partial d_0}{\partial b_2} = -1$$

$$\frac{\partial d_0}{\partial b_3} = -1$$

$$\frac{\partial d_1}{\partial b_2} = 2 - \tau_4 - \tau_6$$

$$\frac{\partial d_1}{\partial b_3} = 2 - \tau_4 - \tau_5$$

$$\frac{\partial d_2}{\partial b_2} = 2\tau_4 + \tau_5 + 2\tau_6 - \tau_4\tau_6$$

$$\frac{\partial d_2}{\partial b_3} = 2\tau_4 + 2\tau_5 + \tau_6 - \tau_4\tau_5$$

$$\frac{\partial d_3}{\partial b_2} = \tau_4\tau_5 + \tau_5\tau_6 + 2\tau_6\tau_4$$

$$\frac{\partial d_3}{\partial b_3} = 2\tau_4\tau_5 + \tau_5\tau_6 + \tau_6\tau_4$$

$$\frac{\partial d_4}{\partial b_k} = \tau_4\tau_5\tau_6$$

$$\frac{\partial x_7}{\partial b_k} = - \frac{\sum_{n=0}^{4} \frac{\partial d_n}{\partial b_k} x_7^{\,n}}{\sum_{n=0}^{4} n d_n x_7^{\,n-1}}$$

$$\frac{\partial F_8}{\partial b_2} = \frac{1 + \tau_4 x_7}{1 + \tau_5 x_7}$$

$$\frac{\partial F_8}{\partial b_3} = \frac{1 + \tau_4 x_7}{1 + \tau_6 x_7}$$

$\partial F_8/\partial x_7$ is computed from equation (A23(a)).

$$\frac{\partial x_8}{\partial b_k} = \frac{1}{F_8}\left(1 - x_8 \frac{\partial F_8}{\partial x_7}\right)\frac{\partial x_7}{\partial b_k} - \frac{x_8}{F_8}\frac{\partial F_8}{\partial b_k}$$

$$\frac{\partial x_9}{\partial b_2} = \frac{b_2\tau_4 x_8 - \tau_5 x_9}{1 + \tau_5 x_7}\frac{\partial x_7}{\partial b_2} + \frac{1 + \tau_4 x_7}{1 + \tau_5 x_7}\left(x_8 + b_2 \frac{\partial x_8}{\partial b_2}\right)$$

$$\frac{\partial x_9}{\partial b_3} = \frac{b_2\tau_4 x_8 - \tau_5 x_9}{1 + \tau_5 x_7}\frac{\partial x_7}{\partial b_3} + \frac{1 + \tau_4 x_7}{1 + \tau_5 x_7} b_2 \frac{\partial x_8}{\partial b_3}$$

$$\frac{\partial x_{10}}{\partial b_2} = \frac{b_3\tau_4 x_8 - \tau_6 x_{10}}{1 + \tau_6 x_7}\frac{\partial x_7}{\partial b_2} + \frac{1 + \tau_4 x_7}{1 + \tau_6 x_7} b_3 \frac{\partial x_8}{\partial b_2}$$

$$\frac{\partial x_{10}}{\partial b_3} = \frac{b_3\tau_4 x_8 - \tau_6 x_{10}}{1 + \tau_6 x_7}\frac{\partial x_7}{\partial b_3} + \frac{1 + \tau_4 x_7}{1 + \tau_6 x_7}\left(b_3 \frac{\partial x_8}{\partial b_3} + x_8\right)$$

$$\frac{\partial x_1}{\partial b_k} = \tau_4\left(\frac{\partial x_8}{\partial b_k} x_7 + x_8 \frac{\partial x_7}{\partial b_k}\right)$$

$$\frac{\partial x_2}{\partial b_k} = \tau_5\left(\frac{\partial x_9}{\partial b_k} x_7 + x_9 \frac{\partial x_7}{\partial b_k}\right)$$

$$\frac{\partial x_3}{\partial b_k} = \tau_6\left(\frac{\partial x_{10}}{\partial b_k} x_7 + x_{10} \frac{\partial x_7}{\partial b_k}\right)$$

The equations for air model D are

$$\frac{\partial d_0}{\partial b_2} = -2$$

$$\frac{\partial d_0}{\partial b_3} = -2$$

$$\frac{\partial d_1}{\partial b_2} = 3 - 2\tau_7 - \tau_8 - 2\tau_9$$

$$\frac{\partial d_1}{\partial b_3} = 3 - 2\tau_7 - 2\tau_8 - \tau_9$$

$$\frac{\partial d_2}{\partial b_2} = 3\tau_7 + 2\tau_8 + 3\tau_9 - \tau_7\tau_8 - \tau_8\tau_9 - 2\tau_9\tau_7$$

$$\frac{\partial d_2}{\partial b_3} = 3\tau_7 + 3\tau_8 + 2\tau_9 - 2\tau_7\tau_8 - \tau_8\tau_9 - 2\tau_9\tau_7$$

$$\frac{\partial d_3}{\partial b_2} = 2\tau_7\tau_8 + 2\tau_8\tau_9 + 3\tau_9\tau_7 - \tau_7\tau_8\tau_9$$

$$\frac{\partial d_3}{\partial b_3} = 3\tau_7\tau_8 + 2\tau_8\tau_9 + 2\tau_9\tau_7 - \tau_7\tau_8\tau_9$$

$$\frac{\partial d_4}{\partial b_k} = 2\tau_7\tau_8\tau_9$$

$$\frac{\partial x_7}{\partial b_k} = - \frac{\sum_{n=0}^{4} \frac{\partial d_n}{\partial b_k} x_7^n}{\sum_{n=0}^{4} n d_n x_7^n}$$

$$\frac{\partial F_{11}}{\partial b_2} = \frac{1 + \tau_7 x_7}{1 + \tau_8 x_7}\left(2 + \tau_8 x_7\right)$$

$$\frac{\partial F_{11}}{\partial b_3} = \frac{1 + \tau_7 x_7}{1 + \tau_9 x_7}\left(2 + \tau_9 x_7\right)$$

$\partial F_{11}/\partial x_7$ is computed from equation (A32(a)).

$$\frac{\partial x_{11}}{\partial b_k} = \frac{1}{F_{11}}\left(1 - \frac{\partial F_{11}}{\partial x_7}\right)\frac{\partial x_7}{\partial b_k} - \frac{x_{11}}{F_{11}} \frac{\partial F_{11}}{\partial b_k}$$

$$\frac{\partial x_{12}}{\partial b_2} = \frac{b_2\tau_7 x_{11} - \tau_8 x_{12}}{1 + \tau_8 x_7} \frac{\partial x_7}{\partial b_2} + \frac{1 + \tau_7 x_7}{1 + \tau_8 x_7}\left(x_{11} + b_2 \frac{\partial x_{11}}{\partial b_2}\right)$$

$$\frac{\partial x_{12}}{\partial b_3} = \frac{b_2\tau_7 x_{11} - \tau_8 x_{12}}{1 + \tau_8 x_7} \frac{\partial x_7}{\partial b_3} + \frac{1 + \tau_7 x_7}{1 + \tau_8 x_7} b_2 \frac{\partial x_{11}}{\partial b_3}$$

$$\frac{\partial x_{13}}{\partial b_2} = \frac{b_3\tau_7 x_{11} - \tau_9 x_{13}}{1 + \tau_9 x_7} \frac{\partial x_7}{\partial b_2} + \frac{1 + \tau_7 x_7}{1 + \tau_9 x_7} b_3 \frac{\partial x_{11}}{\partial b_2}$$

APPENDIX B

$$\frac{\partial x_{13}}{\partial b_3} = \frac{b_3 \tau_7 x_{11} - \tau_9 x_{13}}{1 + \tau_9 x_7} \frac{\partial x_7}{\partial b_3} + \frac{1 + \tau_7 x_7}{1 + \tau_9 x_7} \left(b_3 \frac{\partial x_{11}}{\partial b_3} + x_{11} \right)$$

$$\frac{\partial x_8}{\partial b_k} = \tau_7 \left(\frac{\partial x_7}{\partial b_k} x_{11} + x_7 \frac{\partial x_{11}}{\partial b_k} \right)$$

$$\frac{\partial x_9}{\partial b_k} = \tau_8 \left(\frac{\partial x_7}{\partial b_k} x_{12} + x_7 \frac{\partial x_{12}}{\partial b_k} \right)$$

$$\frac{\partial x_{10}}{\partial b_k} = \tau_9 \left(\frac{\partial x_7}{\partial b_k} x_{13} + x_7 \frac{\partial x_{13}}{\partial b_k} \right)$$

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TABLE I.- SPECIES IN THE AIR MODELS

Model A	Model B	Model C	Model D
N	N	N	N^+
O	O	O	O^+
A	A	A	A^+
N_2	N^+	N^+	N^{++}
O_2	O^+	O^+	O^{++}
NO	e	A^+	A^{++}
	N_2	e	e
	NO		

TABLE II.- NUMBERING OF SPECIES AND REACTIONS

Species		j	Reactions	Mole fraction equilibrium constant, τ_j
i	x_i	1	$2N = N_2$	$\tau_1 = x_4/x_1^2$
1	N	2	$2O = O_2$	$\tau_2 = x_5/x_2^2$
2	O	3	$N + O = NO$	$\tau_3 = x_6/x_1x_2$
3	A	4	$N^+ + e = N$	$\tau_4 = x_1/x_7x_8$
4	N_2	5	$O^+ + e = O$	$\tau_5 = x_2/x_7x_9$
5	O_2	6	$A^+ + e = A$	$\tau_6 = x_3/x_7x_{10}$
6	NO	7	$N^{++} + e = N^+$	$\tau_7 = x_8/x_7x_{11}$
7	e	8	$O^{++} + e = O^+$	$\tau_8 = x_9/x_7x_{12}$
8	N^+	9	$A^{++} + e = A^+$	$\tau_9 = x_{10}/x_7x_{13}$
9	O^+			
10	A^+			
11	N^{++}			
12	O^{++}			
13	A^{++}			
14	NO^+			

TABLE III.- COMPOSITION COMPUTED BY PRESENT METHOD AND COMPOSITION FROM REFERENCE 6

[First value of paired numbers, present method; second value, ref. 6]

(a) Model A

T, °K	$\log_{10}\left(\frac{\rho}{\rho_o}\right)$	N	O	A	N_2	O_2	NO
2000	2	0.2668×10^{-10} $.2668 \times 10^{-10}$	0.1026×10^{-4} $.1025 \times 10^{-4}$	0.9343×10^{-2} $.9343 \times 10^{-2}$	0.7770 .7767	0.2054 .2048	0.8233×10^{-2} $.8219 \times 10^{-2}$
	0	$.2916 \times 10^{-9}$ $.2916 \times 10^{-9}$	$.1109 \times 10^{-3}$ $.1109 \times 10^{-3}$	$.9343 \times 10^{-2}$ $.9340 \times 10^{-2}$	.7769 .7767	.2053 .2052	$.8274 \times 10^{-2}$ $.8270 \times 10^{-2}$
	-2	$.2918 \times 10^{-8}$ $.2917 \times 10^{-8}$	$.1108 \times 10^{-2}$ $.1108 \times 10^{-2}$	$.9339 \times 10^{-2}$ $.9335 \times 10^{-2}$	.7766 .7763	.2047 .2047	$.8259 \times 10^{-2}$ $.8257 \times 10^{-2}$
	-4	$.2903 \times 10^{-7}$ $.2903 \times 10^{-7}$	$.1090 \times 10^{-1}$ $.1090 \times 10^{-1}$	$.9292 \times 10^{-2}$ $.9289 \times 10^{-2}$	.7728 .7725	.1989 .1988	$.8122 \times 10^{-2}$ $.8119 \times 10^{-2}$
	-6	$.2785 \times 10^{-6}$ $.2784 \times 10^{-6}$	$.9270 \times 10^{-1}$ $.9269 \times 10^{-1}$	$.8911 \times 10^{-2}$ $.8906 \times 10^{-2}$	.7415 .7411	.1500 .1500	$.6910 \times 10^{-2}$ $.6908 \times 10^{-2}$
4000	1	0.1210×10^{-3} $.1210 \times 10^{-3}$	0.4399×10^{-1} $.4394 \times 10^{-1}$	$0.9137 + 10^{-2}$ $.9135 \times 10^{-2}$	0.7166 .7163	0.1357 .1354	0.9447×10^{-1} $.9435 \times 10^{-1}$
	0	$.3725 \times 10^{-3}$ $.3724 \times 10^{-3}$	.1172 .1172	$.8794 \times 10^{-2}$ $.8790 \times 10^{-2}$	.6953 .6949	$.9887 \times 10^{-1}$ $.9884 \times 10^{-1}$	$.7947 \times 10^{-1}$ $.7944 \times 10^{-2}$
	-2	$.3392 \times 10^{-2}$ $.3391 \times 10^{-2}$	.3148 .3148	$.7857 \times 10^{-2}$ $.7853 \times 10^{-2}$	.6443 .6439	$.7967 \times 10^{-2}$ $.7970 \times 10^{-2}$	$.2172 \times 10^{-1}$ $.2172 \times 10^{-1}$
	-4	$.3271 \times 10^{-1}$ $.3270 \times 10^{-1}$	.3387 .3388	$.7608 \times 10^{-2}$ $.7604 \times 10^{-2}$	.6185 .6182	$.9526 \times 10^{-4}$ $.9531 \times 10^{-4}$	$.2327 \times 10^{-2}$ $.2327 \times 10^{-2}$
	-6	.2576 .2575	.3017 .3017	$.6730 \times 10^{-2}$ $.6727 \times 10^{-2}$	.4338 .4335	$.8545 \times 10^{-6}$ $.8545 \times 10^{-6}$	$.1846 \times 10^{-3}$ $.1845 \times 10^{-3}$
6000	1	0.1189×10^{-1} $.1189 \times 10^{-1}$	0.2119 .2118	0.8298×10^{-2} $.8294 \times 10^{-2}$	0.6376 .6372	0.3000×10^{-1} $.2997 \times 10^{-1}$	0.1003 .1002
	0	$.3597 \times 10^{-1}$ $.3597 \times 10^{-1}$	.2937 .2937	$.7803 \times 10^{-2}$ $.7798 \times 10^{-2}$	.6122 .6118	$.6049 \times 10^{-2}$ $.6049 \times 10^{-2}$	$.4418 \times 10^{-1}$ $.4416 \times 10^{-1}$
	-2	.2754 .2753	.2955 .2951	$.6677 \times 10^{-2}$ $.6672 \times 10^{-2}$	.4185 .4181	$.7144 \times 10^{-4}$ $.7131 \times 10^{-4}$	$.3969 \times 10^{-2}$ $.3964 \times 10^{-2}$
	-4	.7352 .7338	.2190 .2187	$.4885 \times 10^{-2}$ $.4878 \times 10^{-2}$	$.4078 \times 10^{-1}$ $.4062 \times 10^{-1}$	$.5370 \times 10^{-6}$ $.5355 \times 10^{-6}$	$.1075 \times 10^{-3}$ $.1071 \times 10^{-3}$
8000	2	0.3655×10^{-1} $.3654 \times 10^{-1}$	0.1841 .1834	0.8312×10^{-2} $.8312 \times 10^{-2}$	0.6083 .6079	0.2595×10^{-1} $.2574 \times 10^{-1}$	0.1368 .1362
	0	.2886 .2883	.2806 .2800	$.6684 \times 10^{-2}$ $.6677 \times 10^{-2}$	.4056 .4048	$.6532 \times 10^{-3}$ $.6504 \times 10^{-3}$	$.1788 \times 10^{-1}$ $.1782 \times 10^{-1}$

TABLE III.- COMPOSITION COMPUTED BY PRESENT METHOD AND COMPOSITION FROM REFERENCE 6 – Continued

[First value of paired numbers, present method; second value, ref. 6]

(b) Model B

T, °K	$\log_{10}\left(\frac{\rho}{\rho_o}\right)$	N	O	A	N_2	NO	e^-	N^+	O^+
4 000	-3	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
		0.1056×10^{-1}	0.3371	0.7715×10^{-2}	0.6360	0.7372×10^{-2}	0.1065×10^{-4}	0.3972×10^{-10}	0.3768×10^{-8}
	-4	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
		$.3270 \times 10^{-1}$	.3388	$.7604 \times 10^{-2}$	.6182	$.2327 \times 10^{-2}$	$.1879 \times 10^{-4}$	$.6864 \times 10^{-9}$	$.2115 \times 10^{-7}$
	-6	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
		.2575	.3017	$.6727 \times 10^{-2}$	.4335	$.1845 \times 10^{-3}$	$.5015 \times 10^{-4}$	$.1792 \times 10^{-6}$	$.6241 \times 10^{-6}$
6 000	-1	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
		0.1056	0.3147	0.7374×10^{-2}	0.5563	0.1467×10^{-1}	0.1742×10^{-3}	0.5502×10^{-6}	0.1984×10^{-5}
	-2	.2740	.3012	$.6617 \times 10^{-2}$	.4141	$.4026 \times 10^{-2}$	$.7200 \times 10^{-4}$	$.3091 \times 10^{-4}$	$.4109 \times 10^{-4}$
		.2753	.2951	$.6672 \times 10^{-2}$	.4181	$.3964 \times 10^{-2}$	$.2796 \times 10^{-3}$	$.7998 \times 10^{-5}$	$.1037 \times 10^{-4}$
	-4	.7342	.2186	$.4881 \times 10^{-2}$	$.4066 \times 10^{-1}$	$.1071 \times 10^{-3}$	$.7679 \times 10^{-3}$	$.5645 \times 10^{-3}$	$.2034 \times 10^{-3}$
		.7338	.2187	$.4878 \times 10^{-2}$	$.4062 \times 10^{-1}$	$.1071 \times 10^{-3}$	$.8662 \times 10^{-3}$	$.5002 \times 10^{-3}$	$.1804 \times 10^{-3}$
	-6	.7725	.2072	$.4660 \times 10^{-2}$	$.4717 \times 10^{-3}$	$.1118 \times 10^{-5}$	$.7591 \times 10^{-2}$	$.5732 \times 10^{-2}$	$.1859 \times 10^{-2}$
		.7721	.2074	$.4650 \times 10^{-2}$	$.4712 \times 10^{-3}$	$.1119 \times 10^{-5}$	$.7649 \times 10^{-2}$	$.5685 \times 10^{-2}$	$.1847 \times 10^{-2}$
8 000	0	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
		0.2883	0.2800	0.6677×10^{-2}	0.4048	0.1782×10^{-1}	0.7408×10^{-3}	0.5744×10^{-4}	0.4439×10^{-4}
	-2	.7358	.2166	$.4852 \times 10^{-2}$	$.3624 \times 10^{-1}$	$.4835 \times 10^{-3}$	$.3021 \times 10^{-2}$	$.2448 \times 10^{-2}$	$.5732 \times 10^{-3}$
		.7354	.2166	$.4843 \times 10^{-2}$	$.3620 \times 10^{-1}$	$.4833 \times 10^{-3}$	$.3190 \times 10^{-2}$	$.2317 \times 10^{-2}$	$.5430 \times 10^{-3}$
	-4	.7378	.1994	$.4560 \times 10^{-2}$	$.3878 \times 10^{-3}$	$.4750 \times 10^{-5}$	$.2891 \times 10^{-1}$	$.2379 \times 10^{-1}$	$.5115 \times 10^{-2}$
		.7375	.1996	$.4493 \times 10^{-2}$	$.3874 \times 10^{-3}$	$.4753 \times 10^{-5}$	$.2899 \times 10^{-1}$	$.2371 \times 10^{-1}$	$.5105 \times 10^{-2}$
	-6	.4554	.1293	$.3728 \times 10^{-2}$	$.1808 \times 10^{-5}$	$.2327 \times 10^{-7}$	.2058	.1679	$.3792 \times 10^{-1}$
		.4552	.1294	$.3202 \times 10^{-2}$	$.1806 \times 10^{-5}$	$.2328 \times 10^{-7}$	.2061	.1675	$.3790 \times 10^{-1}$
10 000	0	0.6203	0.2319	0.5321×10^{-2}	0.1304	0.6151×10^{-2}	0.2937×10^{-2}	0.2364×10^{-2}	0.5735×10^{-3}
		.6198	.2312	$.5308 \times 10^{-2}$	.1302	$.6127 \times 10^{-2}$	$.3470 \times 10^{-2}$	$.1999 \times 10^{-2}$	$.4839 \times 10^{-3}$
	-2	.7373	.2010	$.4575 \times 10^{-2}$	.2139	$.7360 \times 10^{-4}$	$.2748 \times 10^{-1}$	$.2335 \times 10^{-1}$	$.4130 \times 10^{-2}$
		.7368	.2011	$.4478 \times 10^{-2}$	.2136	$.7359 \times 10^{-4}$	$.2761 \times 10^{-1}$	$.2323 \times 10^{-1}$	$.4113 \times 10^{-2}$
	-4	.4656	.1376	$.3771 \times 10^{-2}$	$.1035 \times 10^{-4}$	$.3859 \times 10^{-6}$	.1965	.1649	$.3160 \times 10^{-1}$
		.4654	.1377	$.3043 \times 10^{-2}$	$.1034 \times 10^{-4}$	$.3861 \times 10^{-6}$	.1969	.1645	$.3157 \times 10^{-1}$
	-5	.1996	$.6646 \times 10^{-1}$	$.2978 \times 10^{-2}$	$.2408 \times 10^{-6}$	$.1012 \times 10^{-7}$	.3655	.2984	$.6711 \times 10^{-1}$
		.1995	$.6788 \times 10^{-1}$	$.1483 \times 10^{-2}$	$.2406 \times 10^{-6}$	$.1033 \times 10^{-7}$	.3654	.2982	$.6582 \times 10^{-1}$
12 000	0	0.7276	0.2099	0.4770×10^{-2}	0.2809×10^{-1}	0.2077×10^{-2}	0.1382×10^{-1}	0.1180×10^{-1}	0.2021×10^{-2}
		.7268	.2095	$.4703 \times 10^{-2}$	$.2803 \times 10^{-1}$	$.2076 \times 10^{-2}$	$.1423 \times 10^{-1}$	$.1146 \times 10^{-1}$	$.1959 \times 10^{-2}$
	-2	.6060	.1720	$.4184 \times 10^{-2}$	$.2219 \times 10^{-3}$	$.1619 \times 10^{-4}$	.1088	$.9313 \times 10^{-1}$	$.1567 \times 10^{-1}$
		.6057	.1721	$.3674 \times 10^{-2}$	$.2217 \times 10^{-3}$	$.1619 \times 10^{-4}$	.1091	$.9283 \times 10^{-1}$	$.1564 \times 10^{-1}$
	-3	.3807	.1194	$.3529 \times 10^{-2}$	$.1039 \times 10^{-4}$	$.8368 \times 10^{-6}$	.2482	.2093	$.3890 \times 10^{-1}$
		.3805	.1195	$.2359 \times 10^{-2}$	$.1038 \times 10^{-4}$	$.8373 \times 10^{-6}$	.2488	.2087	$.3885 \times 10^{-1}$
14 000	0	0.7088	0.1970	0.4537×10^{-2}	0.6840×10^{-2}	$.8196 \times 10^{-3}$	0.4102×10^{-1}	0.3535×10^{-1}	0.5674×10^{-2}
		.7080	.1967	$.4305 \times 10^{-2}$	$.6825 \times 10^{-2}$	$.8175 \times 10^{-3}$	$.4133 \times 10^{-1}$	$.3505 \times 10^{-1}$	$.5623 \times 10^{-2}$
	-2	.3898	.1224	$.3557 \times 10^{-2}$	$.2637 \times 10^{-4}$	$.3570 \times 10^{-5}$	.2421	.2050	$.3715 \times 10^{-1}$
		.3896	.1225	$.2263 \times 10^{-2}$	$.2635 \times 10^{-4}$	$.3571 \times 10^{-5}$	.2428	.2043	$.3707 \times 10^{-1}$

[a]Wrong root (see text).
[b]No root.

TABLE III.- COMPOSITION COMPUTED BY PRESENT METHOD AND COMPOSITION FROM REFERENCE 6 – Concluded

[First value of paired numbers, present method; second value, ref. 6]

(c) Model C

T, °K	$\log_{10}\left(\frac{\rho}{\rho_0}\right)$	N	O	A	e^-	N^+	O^+	A^+
6 000	-6	0.7731 .7721	0.2071 .2074	0.4650×10^{-2} $.4650 \times 10^{-2}$	0.7596×10^{-2} $.7649 \times 10^{-2}$	0.5732×10^{-2} $.5685 \times 10^{-2}$	0.1857×10^{-2} $.1847 \times 10^{-2}$	0.7997×10^{-5} $.7942 \times 10^{-5}$
8 000	-4	0.7383 .7375	0.1993 .1996	0.4494×10^{-2} $.4493 \times 10^{-2}$	0.2894×10^{-1} $.2899 \times 10^{-1}$	0.2377×10^{-1} $.2371 \times 10^{-1}$	0.5106×10^{-2} $.5105 \times 10^{-2}$	0.6409×10^{-4} $.6398 \times 10^{-4}$
	-6	.4554 .4552	.1293 .1294	$.3204 \times 10^{-2}$ $.3202 \times 10^{-2}$	.2060 .2061	.1676 .1675	$.3787 \times 10^{-1}$ $.3790 \times 10^{-1}$	$.5226 \times 10^{-1}$ $.5221 \times 10^{-3}$
10 000	-3	0.6558 .6553	0.1818 .1820	0.4044×10^{-2} $.4043 \times 10^{-2}$	0.7916×10^{-1} $.7920 \times 10^{-1}$	0.6686×10^{-1} $.6677 \times 10^{-1}$	0.1203×10^{-1} $.1203 \times 10^{-1}$	0.2777×10^{-3} $.2775 \times 10^{-3}$
	-4	.4657 .4654	.1375 .1377	$.3045 \times 10^{-2}$ $.3043 \times 10^{-2}$	.1969 .1969	.1646 .1645	$.3154 \times 10^{-1}$ $.3157 \times 10^{-1}$	$.7249 \times 10^{-3}$ $.7244 \times 10^{-3}$
	-6	$.3913 \times 10^{-1}$ $.3911 \times 10^{-1}$	$.1539 \times 10^{-2}$ $.1541 \times 10^{-2}$	$.3323 \times 10^{-3}$ $.3321 \times 10^{-3}$	.4726 .4726	.3748 .3746	$.9564 \times 10^{-1}$ $.9574 \times 10^{-1}$	$.2143 \times 10^{-2}$ $.2142 \times 10^{-2}$
12 000	-2	0.6063 .6057	0.1719 .1721	0.3675×10^{-2} $.3674 \times 10^{-2}$	0.1091 .1091	0.9294×10^{-1} $.9283 \times 10^{-1}$	0.1563×10^{-1} $.1564 \times 10^{-1}$	0.5068×10^{-3} $.5066 \times 10^{-3}$
	-4	.1299 .1298	$.4927 \times 10^{-1}$ $.4932 \times 10^{-1}$	$.8370 \times 10^{-3}$ $.8365 \times 10^{-3}$	.4100 .4100	.3331 .3330	$.7493 \times 10^{-1}$ $.7501 \times 10^{-1}$	$.1932 \times 10^{-2}$ $.1931 \times 10^{-2}$
	-6	$.2212 \times 10^{-2}$ $.2211 \times 10^{-2}$	$.9970 \times 10^{-3}$ $.9980 \times 10^{-3}$	$.1470 \times 10^{-4}$ $.1468 \times 10^{-4}$	.4984 .4984	.3914 .3912	.1046 .1047	$.2340 \times 10^{-2}$ $.2337 \times 10^{-2}$
14 000	-1	0.6084 .6074	0.1728 .1729	0.3597×10^{-2} $.3598 \times 10^{-2}$	0.1076 .1076	0.9195×10^{-1} $.9181 \times 10^{-1}$	0.1508×10^{-1} $.1509 \times 10^{-1}$	0.5912×10^{-3} $.5914 \times 10^{-3}$
	-2	.3898 .3896	.1224 .1225	$.2264 \times 10^{-2}$ $.2263 \times 10^{-2}$	.2428 .2428	.2044 .2043	$.3704 \times 10^{-1}$ $.3707 \times 10^{-1}$	$.1291 \times 10^{-2}$ $.1290 \times 10^{-2}$
	-4	$.2287 \times 10^{-1}$ $.2286 \times 10^{-1}$	$.1021 \times 10^{-1}$ $.1022 \times 10^{-1}$	$.1264 \times 10^{-3}$ $.1263 \times 10^{-3}$	.4834 .4834	.3826 .3823	$.9855 \times 10^{-1}$ $.9865 \times 10^{-1}$	$.2298 \times 10^{-2}$ $.2296 \times 10^{-2}$
	-6	$.2539 \times 10^{-3}$ $.2533 \times 10^{-3}$	$.1180 \times 10^{-3}$ $.1181 \times 10^{-3}$	$.1397 \times 10^{-5}$ $.1357 \times 10^{-5}$	.4998 .5002	.3923 .3910	.1052 .1052	$.2346 \times 10^{-2}$ $.2278 \times 10^{-2}$

(d) Model D

T, °K	$\log_{10}\left(\frac{\rho}{\rho_0}\right)$	e^-	N^+	O^+	A^+	N^{++}	O^{++}	A^{++}
13 000	-6	0.5001 .4996	0.3922 .3917	0.1052 .1051	0.2336×10^{-2} $.2333 \times 10^{-2}$	0.1060×10^{-3} $.1059 \times 10^{-3}$	0.6773×10^{-6} $.6770 \times 10^{-6}$	0.1027×10^{-4} $.1026 \times 10^{-4}$
14 000	-6	0.5004 .5002	0.3913 .3910	0.1052 .1052	0.2279×10^{-2} $.2278 \times 10^{-2}$	0.7689×10^{-3} $.7687 \times 10^{-3}$	0.6957×10^{-5} $.6962 \times 10^{-5}$	0.6555×10^{-4} $.6554 \times 10^{-4}$
15 000	-5	0.5002 .4995	0.3918 .3911	0.1052 .1050	0.2311×10^{-2} $.2308 \times 10^{-2}$	0.4370×10^{-3} $.4369 \times 10^{-3}$	0.5314×10^{-5} $.5312 \times 10^{-5}$	0.3439×10^{-4} $.3439 \times 10^{-4}$
	-6	.5023 .5022	.3863 .3861	.1047 .1048	$.2038 \times 10^{-2}$ $.2036 \times 10^{-2}$	$.4242 \times 10^{-2}$ $.4240 \times 10^{-2}$	$.5208 \times 10^{-4}$ $.5213 \times 10^{-4}$	$.2985 \times 10^{-3}$ $.2983 \times 10^{-3}$

TABLE IV.- $\partial d_n / \partial \tau_j$ FOR MODEL A

n \ j	1	2	3
0	$-\frac{b_2^2}{\tau_1^2}$	0	0
1	$\frac{b_2}{\tau_1^2}(\gamma_2 - \gamma_1)$	0	$\frac{b_2}{\tau_1}(\gamma_0 - 1)$
2	$\frac{b_2\gamma_3 + \gamma_1\gamma_2}{\tau_1^2}$	$-b_2\left[8(\gamma_0 - b_2) + \frac{2 + b_2 + b_3}{\tau_1}\right]$	$-\frac{1}{\tau_1}\left[b_2(b_2 + b_3) + (\gamma_0 - b_2)\right] \times \left[1 + b_2 + b_3 + 2\tau_3(1 - b_2)\right]$
3	$\frac{\gamma_1}{\tau_1^2}(b_2\tau_2 + \gamma_3)$	$4\gamma_0(\gamma_0 - b_2) - \frac{2\gamma_1}{\tau_1}(1 + b_2 + b_3)$	$-\frac{1}{\tau_1}\left[2\gamma_1(b_2 + b_3) + \gamma_4(1 + b_2 + b_3)\right]$
4	$\frac{\gamma_1^2\tau_2}{\tau_1^2}$	$(\gamma_0 - b_2)^2\left(8\tau_2 - \frac{\tau_3^2}{\tau_1}\right)$	$-\frac{\gamma_1\gamma_4}{\tau_1}$

TABLE V.- $\partial d_n / \partial \tau_j$ FOR MODEL C

n \ j	4	5	6
0	0	0	0
1	$-(b_2 + b_3)$	$-(1 + b_3)$	$-(1 + b_2)$
2	$1 + 2(b_2 + b_3) - b_2\tau_6 - b_3\tau_5$	$2 + b_2 + 2b_3 - \tau_6 - b_3\tau_4$	$2 + 2b_2 + b_3 - \tau_5 - b_2\tau_4$
3	$(1 + b_2 + 2b_3)\tau_5 + (1 + 2b_2 + b_3)\tau_6$	$(1 + b_2 + 2b_3)\tau_4 + (2 + b_2 + b_3)\tau_6$	$(2 + b_2 + b_3)\tau_5 + (1 + 2b_2 + b_3)\tau_4$
4	$(1 + b_2 + b_3)\tau_5\tau_6$	$(1 + b_2 + b_3)\tau_4\tau_6$	$(1 + b_2 + b_3)\tau_4\tau_5$

TABLE VI.- $\partial d_n / \partial \tau_j$ FOR MODEL D

n \ j	7	8	9
0	0	0	0
1	$-(1 + 2b_2 + 2b_3)$	$-(2 + b_2 + 2b_3)$	$-(2 + 2b_2 + b_3)$
2	$(2 + 3b_2 + 3b_3)$ $- \tau_8(1 + b_2 + 2b_3)$ $- \tau_9(1 + 2b_2 + b_3)$	$(3 + 2b_2 + 3b_3)$ $- \tau_7(1 + b_2 + 2b_3)$ $- \tau_9(2 + b_2 + b_3)$	$(3 + 3b_2 + 2b_3)$ $- \tau_8(2 + b_2 + b_3)$ $- \tau_7(1 + 2b_2 + b_3)$
3	$\tau_8(2 + 2b_2 + 3b_3)$ $+ \tau_9(2 + 3b_2 + 2b_3)$ $- \tau_8\tau_9(1 + b_2 + b_3)$	$\tau_7(2 + 2b_2 + 3b_3)$ $+ \tau_9(3 + 2b_2 + 2b_3)$ $- \tau_7\tau_9(1 + b_2 + b_3)$	$\tau_8(3 + 2b_2 + 2b_3)$ $+ \tau_7(2 + 3b_2 + 2b_3)$ $- \tau_7\tau_8(1 + b_2 + b_3)$
4	$2\tau_8\tau_9(1 + b_2 + b_3)$	$2\tau_7\tau_9(1 + b_2 + b_3)$	$2\tau_7\tau_9(1 + b_2 + b_3)$

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